

Reply to Reviewer 1

We thank Professor Algeo for his time and providing helpful comments. We have replied to each point in the review here and will submit a revised manuscript that combines comments from all reviewers once all reviews have been completed. Please find our point to point reply below. Text from the review is in blue and our replies are in black.

Overall, this study is very well-executed, and the interpretations and conclusions are quite reasonable. It should become acceptable for publication following minor revision. I offer some insights on a few important issues as well as some minor comments that the authors should consider during the revision stage.

The approach adopted in this study is to be commended in one respect in particular: It is useful to identify the main components of a sample set, and to link the geochemistry of the bulk samples to these components. This should be self-evident, but too frequently geochemical proxies are interpreted in chemostratigraphic studies with little consideration given to the underlying host sediment fractions.

Thank you. A key aim of this study was to use petrographic information to support geochemical interpretation.

Major issues:

1) Flux calculations should be presented for arguments that invoke sediment fluxes. For example: Page 8, line 31: "The fine-grained nature of the sedimentary rock may indicate a siliciclastic starvation process." When making claims regarding high or low siliciclastic or organic fluxes, it is generally a good idea to support them with some actual flux calculations. Making reliable flux calculations may be difficult for poorly dated formations, but the present study units are exceedingly well-dated, spanning the Pectinatites wheatleyensis to Pectinatites pectinatus ammonite biozones. This interval corresponds to 1.5 Myr (ca. 151.2-149.7 Ma) per the 2012 Geologic Time Scale (Gradstein et al., 2012, chapter 26). The study interval comprises 45 m, so its average sedimentation rate is 30 m/Myr—in other words, a pretty average cratonic rate. There might be condensed intervals within this succession, but it is not sediment-starved as a whole, as implied by the statement above.

We fully agree that flux rates are easy to include and add value to the manuscript. We have incorporated flux rates into the revised manuscript and have reworded the text to remove the siliciclastic starvation reference.

Page 9, line 8: "the occurrence of normally graded beds with erosional bases in TOC- rich sections of the HVMI indicates an energetically dynamic setting." A combination of high energy levels and sediment starvation would produce a lag deposit, i.e., concentrated high-density and/or resistant clasts such as fossil, pyrite, and/or phosphate grains. Are there any features of this type in the study succession?

We do not see evidence of lag deposits. Given the calculation of the flux rates, it is unlikely that the system was sediment starved so this is not unexpected. We have added another figure to the revised manuscript containing optical light and SEM images to further illustrate our sedimentary descriptions.

Page 9, line 31: "Based on the chronostratigraphic time frame for the Yorkshire and Dorset sections (Armstrong et al., 2016; Huang et al., 2010) . . ." If there is a published astrochronology for the study formations (Huang et al., 2010), why not integrate it into the present study and discuss its implications for the duration and accumulation rates of these formations?

We agree that an astrochronological framework would be useful in investigating different flux rates; however, the existing framework is based on a laterally (more or less) equivalent section and assumes continuous sedimentation. We have petrographic evidence that there is sediment missing from the section (e.g. erosional surfaces). Furthermore, we do not have enough data for a statistically robust examination of astrochronological cycles in the Yorkshire section (i.e., the section is too short and does not contain enough cycles). Therefore, we feel transferring the astrochronological framework from the Dorset section to the Yorkshire section introduces large uncertainties. Nevertheless, we have included the framework for reference and have discussed the strengths and weaknesses of this approach in the revised manuscript.

2) Interpretation of controls on high TOC or high CaCO₃ intervals:

Page 10, line 24: “We therefore propose that nutrient availability was the likely driver of changes in productivity. . . . The wet-dry cycles proposed by recent climate modelling (Armstrong et al., 2016) may therefore be the key driver behind oscillations in the production and preservation of TOC, i.e. the switching between the LVMI and HVMI.” This is certainly possible but might be difficult to prove. An alternative hypothesis is that organic productivity and sinking fluxes were held more-or-less constant, and the large variations in TOC content were driven by variable influx of siliciclastics, leading to variable dilution of the organic carbon flux. Perhaps the authors could provide arguments countering this alternative hypothesis? Of course, it is also possible that both nutrient and siliciclastic fluxes were covarying in tandem.

We agree that this is an alternative hypothesis but do not have the data to distinguish between the two. We have updated the manuscript to reflect this.

Here is where the astrochronology of the study formations might help—if a characteristic periodic signal (e.g., 100-kyr eccentricity cycles) is present, then it is potentially possible to calculate short-term variations in sedimentation rates in a study section, rather than being limited to an average sedimentation rate for the entire section (as calculated above). An example of application of a floating time scale to analysis of short-term sedimentation rate variation is given in Algeo et al. 2011 (Algeo, T.J., Kuwahara, K., Sano, H., Bates, S., Lyons, T., Elswick, E., Hinnov, L., Ellwood, B., Moser, J. and Maynard, J.B., 2011. Spatial variation in sediment fluxes, redox conditions, and productivity in the Permian–Triassic Panthalassic Ocean. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 308(1-2), pp. 65-83.).

The astrochronological framework was built upon the laterally equivalent type section in Dorset and assumes continuous sedimentation, therefore we do not feel it would be appropriate to calculate rates of short-term variation using astrochronology from a different section.

Page 10, line 30: “Carbonate productivity, mainly in the form of coccoliths, varies throughout the studied KCF section and is at its maximum within the carbonate-rich sections of the HVMI.” Probably correct, but again this represents an assumption, not a proven fact, and one could argue (as for TOC variations; see above) that variable siliciclastic influence controlled variations of carbonate content in the study section.

We agree and have included alternative hypothesis in the revised manuscript.

Page 11, line 13: “However, enrichment factors of redox sensitive trace elements (Mo and U; Fig. 8) ... indicate that during the deposition of the LVMI, the sediment pore water was suboxic to anoxic.” This is open to interpretation, but my opinion is that the modest Mo-EFs (mean 4, max 20) and U-EFs (mean 2, max 4) of the LVMI indicate overwhelmingly suboxic conditions. These values are not strongly supportive of anoxic conditions.

We agree. We have updated the manuscript accordingly.

Section 5.3.4: One point about particulate shuttles that is not made clearly here is that they seem to be most effective at authigenic trace metal enrichment when redox conditions fluctuate strongly, as opposed to stably euxinic conditions (see Algeo and Tribovillard, 2009).

We have updated the manuscript accordingly.

3) Minor issues:

Page 9, line 14: "Owing to the shallow gradients and vast extent of epicontinental seaways, sediment dispersal in the LVMI, which are dominated by terrigenous mud, is likely to have been controlled by wind- and tide-induced bottom currents (Schieber, 2016)." Whether winds and tides could induce significant bottom currents would depend on water depths—at tens of meters, they would be important but at hundreds of meters much less so. The geologic background section (page 3, line 30) indicates considerable uncertainty regarding water depths in the NW European Sea, so the potential influence of bottom currents is uncertain.

We have updated the manuscript to reflect this.

Page 10, line 5: "Biological components (coccolithophores, foraminiferans, and organic carbon) occur in differing proportions throughout the section (Figs. 2 and 3). Our petrographic observations (Fig. 2)..." The presented petrographic data appear to be entirely visual/descriptive. Why not undertake point counts of organic maceral types? This would provide more quantitative information about the nature of the organic fraction that could be compared with other data (e.g., $\delta^{13}\text{C}$ -org)

Given the fine-grained nature of the sediment, point counting these samples would have to be done under SEM, where organic matter type could not be determined. Instead, we have further and more fully integrated published RockEval data that provides information on organic matter type.

Page 10, line 22: "Water depth is not likely to have exceeded a few hundreds of meters in the distal Cleveland Basin (Bradshaw et al., 1992), suggesting that the euphotic zone could have reached the seafloor and light did not limit primary productivity." This statement betrays an incomplete understanding of the photic zone. Light intensity is attenuated quickly and drops to 30% of surface levels by 10 m and to a few percent by 100 m water depth in clear water; in turbid water, the rate of attenuation can be much faster with depth. Most primary productivity is typically in the upper 10 m of the water column, and there will be very little productivity at the depths suggested here.

We have adjusted the text to reflect this in the revised manuscript.

Page 14, line 32: "we can confirm that the repeated development of anoxic/euxinic conditions in the distal Cleveland Basin was most likely due to high primary productivity, and possibly salinity stratification due to high amounts of freshwater runoff". We encourage the authors to investigate the use of paleosalinity proxies to evaluate changes in freshwater runoff in this depositional system. Check this paper for paleosalinity analysis techniques:

Wei, W., Algeo, T.J., Lu, Y., Lu, Y., Liu, H., Zhang, S., Peng, L., Zhang, J. and Chen, L., 2018. Identifying marine incursions into the Paleogene Bohai Bay Basin lake system in northeastern China. *International Journal of Coal Geology*, 200, pp. 1-17.

We have looked at the suggested paleosalinity proxies and they do not show systematic variations, most likely indicating that the system was marine at all times.

Page 15, line 14: “The HVMI in the present study bear similarities to the Gulf of California in that they exhibit similarities in Cd enrichment and Mn depletion”. The 2016 study by Tim Sweere is highly relevant in this regard and should be cited:

Sweere, T., van den Boorn, S., Dickson, A.J. and Reichart, G.J., 2016. Definition of new trace-metal proxies for the controls on organic matter enrichment in marine sediments based on Mn, Co, Mo and Cd concentrations. *Chemical Geology*, 441, pp.235-245.

This reference has been added to the manuscript.

Page 16, line 2: “While the studied interval shares similarities and differences with both upwelling and anoxic basin type settings, we are still lacking an appropriate modern analogue. Palaeogeography exerts a fundamental control on sedimentation, in particular, TOC enrichment, but there is no modern-day example of a shallow epicontinental seaway.” Agreed, but the authors should consider the examples provided in Algeo et al. (2008):

Algeo, Thomas J., Philip H. Heckel, J. Barry Maynard, Ronald C. Blakey, Harry Rowe, B.R. Pratt, and C. Holmden. "Modern and ancient epeiric seas and the super-estuarine circulation model of marine anoxia." *Dynamics of Epeiric Seas: Sedimentological, Paleontological and Geochemical Perspectives: Geological Association Canada Special Paper 48 (2008): 7-38.*

This reference has been added to the manuscript

Reply to Reviewer 2

We thank Dr McKay for her time and detailed review, which has certainly improved our manuscript. Please find our point-to-point reply below. Text from the review is in blue and our replies are in black.

This manuscript uses a wide variety of geochemical proxies, which they integrate with sedimentological information, to investigate the depositional environment of the Kimmeridge Clay Formation in the Cleveland Basin. In general, the conclusions they reach are valid and after some moderate revisions I recommend publication of this manuscript.

Important revisions:

1. Section 3 (Materials and methods) should include information about precision and accuracy, as well as better descriptions of the analytical methods; notably for the analysis of carbon isotopes. Details are provide below.
2. The manuscript is a bit disorganized in places (e.g., interpretations more suited to the discussion are found within the result section, figures are out of order). Details are provided below.
3. The discussion of the d13Corg data is limited and lacking in detail. The authors simply say lighter values indicate more terrestrial organic matter. While this is correct they do not providing references / background information to support this interpretation. In general, Section 5.2 is lacking in appropriate references.

The important revisions listed above are expanded upon in specific comments section so they are addressed below.

Specific Comments:

Page 1, Line 27 – You talk about “three states that produced a distinct cyclicity” however the paper is primarily divided into two units LVMI and HVMI. This is a bit confusing.

We have rephrased this to explain that that HVMI comprise carbonate-rich and organic carbon-rich units.

Page 3, Lines 27 and 28 – Why are “ocean overturn, salinity/temperature stratification and redox conditions” mentioned in this sentence about organic carbon enrichment? Something does not make sense here.

We have reworded this to make it clearer.

Page 4, line 13 – The sediments might be thermally immature but 425°C is high and would have undoubtedly affected the sediments. Diagenetic alteration can occur at temperatures below 100°C. Just something to keep in mind especially when looking at the Hg data.

We agree. We have added a sentence to consider this. Ongoing research suggests thermal maturity would affect Hg contents depending upon which sedimentary component hosts the Hg. i.e. if the Hg resides in the pyrite, it may be less susceptible to diagenetic alteration (Them et al., 2019).

T.R. Them, C.H. Jagoe, A.H. Caruthers, B.C. Gill, S.E. Grasby, D.R. Gröcke, R. Yin, J.D. Owens, Terrestrial sources as the primary delivery mechanism of mercury to the oceans across the Toarcian Oceanic Anoxic Event (Early Jurassic), *Earth and Planetary Science Letters*, Volume 507, 2019, Pages 62-72, ISSN 0012-821X, <https://doi.org/10.1016/j.epsl.2018.11.029>.

Section 3, General comment – Where is the information about precision and accuracy of the geochemical analyses?

We have added this to Supplement A.

Page 4, line 20 – It is highly unlikely that sedimentation was linear throughout this time period. The changes in climate and resulting changes in sedimentation were simply too drastic. It would be better to use the biostratigraphy to estimate how much time this covers.

Biostratigraphy has been used to calculate sedimentation rate. We have expanded upon the calculation of linear sedimentation rates and the associated problems.

Page 4, line 28 – XRF measures major and minor (not trace) elements. For consistency, you should also list which elements were analysed

We have listed the elements that were analysed in the revised manuscript.

Page 4, lines 28 to 29 – More information about how $\delta^{13}\text{C}_{\text{org}}$ was measured is needed. What equipment was used? Were the samples pretreated to remove carbonate before $\delta^{13}\text{C}$ was analyzed? What standards were analyzed?

This information is available in Supplement A, but we have moved it into the manuscript for clarity.

Page 5, lines 9 to 15 – This discussion about Hg does not belong here. Move to page 8 (First paragraph of the discussion).

We have made this revision.

Page 5, line 17 – You need to provide more detail on how the boundaries of the HVMI were determined. I'm requesting this because the lowermost zone is thicker than I think it should be based on carbonate and $\delta^{13}\text{C}_{\text{org}}$ values.

The HVMI is defined as intervals in which carbonate and organic carbon contents are highly variable, thus the lowermost HVMI is the correct thickness as it incorporates the exceptionally high TOC values. We have added a sentence to clarify this in the manuscript.

Page 6, lines 2 and 3 – Did you measure grain sized? If not, how are you determining the difference between “medium to coarse mud-size” and “fine to coarse mud-sized”? Also, there is technically no such thing as a “mud-sized grain”. Grain size is subdivided into clay, silt and sand . . . mud is a mix of clay and silt, with perhaps a bit of fine sand.

Grain size was measured on the SEM using a ruler in the AZTEC software (used to run the SEM). We choose to use the Lazar et al 2015 classification system where sand is defined as any grain between 62.5 μm and 2000 μm , coarse mud is between 62.5 μm and 32 μm , medium mud is between 32 μm and 8 μm and fine mud is anything less than 8 μm . See Lazar et al 2015 for detailed discussion. We have added a sentence to the manuscript to clarify this.

Page 6, lines 11 and 12 – According to what you wrote at the end of page 5 LVMI are composed of two facies (1 and 6) so facies 4 should be discussed in Section 4.1.2

We have moved the discussion of facies 4 to Section 4.1.2.

Page 6, line 16 – What three samples are you referring to in Figure 2? I assume it is those samples identified by arrows but you should make this clear by saying (Fig 2, arrows in CaCO_3 plot).

We have made this revision.

Page 6, lines 20 to 30 – You need to emphasize the differences between Facies 2 and 3. It would help if you referred to Figure 3 more often throughout Section 4.1.

We have made this revision.

Pages 7 and 8 – Section 4.2 should simply describe the results. For example, LVMI have lower $\delta^{13}\text{C}_{\text{org}}$ values than the HVMI (Fig. 2). The interpretation of the $\delta^{13}\text{C}$ data should not occur until the Discussion. Furthermore, a lot of the results are not mentioned (e.g., CaCO_3 content in the LVMI). This section needs to be cleaned up.

We have rewritten this section to address this comment.

Page 7, lines 18 to 20 – This discussion about the $\delta^{13}\text{C}_{\text{org}}$ data needs to move to Section 5. Once you do this, please provide references for this statement “Marine organic matter has a higher $\delta^{13}\text{C}_{\text{org}}$ than terrestrial OM”.

We have made this revision in the revised manuscript and an added appropriate reference to support the statement.

Page 8, line 24 – You need to better explain how Hg/TOC data rules out a volcanogenic sediment source. Also, these sediments got rather warm during burial (425°C) ... would this affect the Hg content?

We have expanded upon the explanation of Hg/TOC as a proxy and commented on the expected effect of thermal maturity on Hg contents.

General comment about Discussion – Section 5.1 merges a lot of information, much of which you haven't discussed yet (e.g., the $\delta^{13}\text{C}_{\text{org}}$ data which is, or should be, discussed in section 5.2). I suggest you swap the order of sections 5.1 and 5.2 (i.e., discuss productivity and organic carbon first).

We agree that this would improve clarity so have made this change in the revised manuscript.

Page 8, line 30 – You cannot identify what clay minerals are present (i.e., kaolinite vs illite) using just petrography. This requires specialized X-ray diffraction techniques.

Low resolution XRD data was published from the Ebberston 87 Core by Herbin et al. (1991). We have included this work in the revised manuscript.

Page 10, Section 5.2 – This section might be easier to understand if you divided into subsections as you did for Section 5.3 (i.e., a subsection for LVMIs and HMVIs).

We agree that this improves clarity so have made this revision.

Page 10, line 7 – A brief discussion about what type II and III organic matter is would be helpful. Also, this is the place to discuss how $\delta^{13}\text{C}_{\text{org}}$ can be used to identify terrestrial vs marine organic matter. Can you estimate the end member marine and terrestrial values? If yes, you could estimate the fraction of organic matter that is terrestrial vs marine. I assume you do not have %N data but if you did you could also use Corg/N ratios . . . although not all terrestrial organic matter has high Corg/N ratios.

We have expanded upon the discussion on use of $\delta^{13}\text{C}_{\text{org}}$ as a proxy for organic matter type.

Page 10, line 11 – So, if the LVMIs are deposited in a more “distal” location relative to the HMVIs . . . why is terrestrial organic matter higher in the LVMIs?

Given the epicontinental seaway setting, we have removed the terms ‘proximal’ and ‘distal’ from the manuscript as they are unlikely to be very apparent in the fine-grained sedimentary record (owing to the shallow gradients).

Page 10, line 23 – It is extremely unlikely that the euphotic zone reached the seafloor if waters depths were greater than 200 meters, which is the approximate limit of the euphotic zone in the modern ocean. That said, light limitation would only be an issue in at higher latitudes (i.e., mid-latitudes to polar regions) where in winter it limits productivity along with strong storm mixing. Nutrient supply is undoubtedly controlling productivity.

We agree and have revised that paragraph to reflect this.

Page 11, lines 1 and 2 – I agree that nutrient availability may have influenced whether the HVMI sediments were TOC-rich or carbonate-rich. In the modern ocean, a well- stratified water column, characterized by a stable, warm, nutrient-poor surface layer does favor coccolithophorids over diatoms.

We are pleased that the reviewer supports our interpretation.

Page 11, line 4 – The discussion about fecal pellets and zooplankton is not critical to the discussion and perhaps distracting. I suggest removing it. If you prefer to keep it then write it in the same way as it is written on page 17 and include some references that support the idea that packaging of organic matter into fecal pellets speeds the delivery to the seafloor and aids in preservation. Also, zooplankton were probably around during the formation of both LVMIs and HMVIs . . . but bioturbation of the LVMIs destroyed the

fecal pellets in these units. Interestingly, in modern sediments fecal pellets tend to be preserved where you have sediment starvation regardless of whether there is bioturbation or not.

We have added appropriate references to support our statement.

Page 11, lines 12 and 13 – In section 4.2.1 (page 7, line 25) you mention that trace metal enrichments in LVMI are low (i.e., around 1) which agrees with metal/Al ratios shown in Figure 6. However, here you say there are trace metal enrichments and imply they are large. What I believe you mean to say is that when you look at Mo and U EFs (Fig 8 . . . which should be Fig 7) there is some enrichment indicating the development of reducing conditions after burial. Please clarify.

We have corrected this in the revised manuscript.

Figures 7 and 8 – you need to switch the order of Figures 7 and 8 so they match the order they are discussed in the text. Make sure to change the figure numbers in the text as well. Also, the figure caption for Fig 8 (what will be Fig 7) has some errors (e.g., the panels that depict the HVMI are blue not grey).

We have made this revision.

Page 11, lines 16 to 24 – this discussion about TOC should be moved to Section 5.2 (i.e., the Productivity and organic matter composition).

We have made this revision.

Page 11, line 25 - I think you mean HVMI . . . not LVMI in the title of section 5.3.2

We have made this revision.

Page 11, line 28 – technically anoxic refers to porewaters with sulfide and euxinic to a water column (i.e., bottom waters) with sulfide but I know there is some “debate” about these terms.

We define ‘anoxic’ as water depleted of oxygen and ‘euxinic’ as water depleted of oxygen and with free H₂S, these definitions are irrespective of depth.

Page 12, lines 4 and 5 – You still have not discussed Figure 7 and you are now mentioning Figure 9. I would remove this sentence and wait until Section 5.3.4 to discuss it.

We agree this improves the manuscript and have made this revision in the manuscript.

Page 12, lines 6 to 9 – I agree, what you are seeing in the KCF looks very similar to the Baltic Sea.

We are pleased that the reviewer supports our interpretation.

Page 12, line 27 – Do you mean that the high As/Al and Sb/Al ratios within the HVMI support the idea of higher pyritisation? A better way of saying this is that pyritization probably explains the enrichment of metals known to accumulate with pyrite (e.g., As, Sb and Mo).

We do mean this so have reworded this sentence to the suggestion made.

Page 13, line 12 to 13 – You need to emphasize that those steep geochemical gradients are driven by changes in oxygen vs sulfide (i.e., redox).

We agree and have done this in the revised manuscript.

Page 13, line 16 – replace the word “phases” with “particulates” at both the start and end of this line.

We have done this in the revised manuscript.

Page 13, line 24 – You need to explain the Mn better (e.g., what about the Mn carbonates). I suggest removing this sentence and adding a paragraph about Mn at the end of this section.

We have done this in the revised manuscript.

Page 14, lines 4 and 5 – remove “with associated enrichments of redox sensitive/sulfide forming trace metals (Fig. 6)” . . . it is not needed here.

We have done this in the revised manuscript.

Page 14, lines 6 to 8 – Also remove this sentence. It does not read well and you basically say the same thing in the next paragraph. So, now you can merge the second and third paragraphs on this page.

We have done this in the revised manuscript.

Page 14, line 19 – Can you provide some Mo/U enrichment ratio data for other rock and sediments (not just the Tribovillard et al 2012 data which is also the KCF) to support your conclusion that the Mn-Fe shuttle must have been working during HVMI deposition. A figure similar to your Figure 9 would work. If there are not enough data to do this, you need to say “probably facilitated”.

The Mn-Fe shuttle is identified in a number of deposits besides the KCF so we will mention this and provide references in the revised manuscript.

Page 14, lines 26 and 27 – I’m not sure what you mean by “which is in good agreement with our Fe/Al and Mn/Al data discussed above”. I’d remove this.

We have done this in the revised manuscript.

Page 14, line 28 – didn’t you say sediment redox conditions in the LVMI become anoxic (Page 11, line 14)? It cannot be both.

We have removed ‘or anoxic’ from Page 11, line 14.

Page 15, line 5 – no need to reference Brumsack (2006) here.

We have removed this reference.

Page 15, line 6 – average shale or UCC?

In section 5.3.5, enrichment factors are calculated to average shale to facilitate direct comparison with the Brumsack (2006) compilation.

Page 15, line 15 – I thought that Mn (in the form of carbonate) was enriched in the HVMI (Page 12, line 1). Perhaps depletion is not the correct word or you need to clarify “depleted in comparison to . . .”.

We have replaced ‘depletion’ with ‘depleted in comparison to the HVMI’.

Page 15, line 25 – by “the two intervals of deposition” are you referring to the Black Sea and HVMI? This is unclear.

We do and have reworded to clarify this point.

Page 16, line 4 – What do you mean by “If at all...”? Are you trying to suggest the Baltic is the best modern analogue we have? Right, I see where you say this on line 16. Perhaps you need to move this last paragraph (lines 16 to 21) up to line 4.

We have done this in the revised manuscript.

Page 16, lines 23 to 16 – You repeat yourself a couple of times. This paragraph needs to be rewritten or just remove it.

We have rewritten to remove the repetition.

Page 16, line 18 – rewrite as follows “. . .fluctuated between LVMI and HVMI deposition.”

We have done this in the revised manuscript.

Page 16, line 10 – I thought you said high TOC concentrations related to the fact it was terrestrial. Where did you say that reducing conditions lead to TOC enrichment in the LVMI?

TOC in the LVMI is predominantly terrestrial organic matter, the preservation of which is facilitated by suboxic sediment-water interface conditions.

Page 17, general comments – do fluctuations in sea level not play a role in the changes we are seeing?

Previous work (e.g. Herbin et al., 1993) indicates that sea level is not the primary control on organic carbon enrichment in the studied interval.

Page 17, line 4 – write as follows “an increase in OM flux rate to the seafloor”

We have done this in the revised manuscript.

Page 17, line 7 – you mention elevated depositional energies during the during oxygenation events associated with HVMI but in Figure 3 the erosional features are associated with Facies 2, which I thought was the “anoxic” facies. Please clarify.

The different scales of petrography and bulk rock geochemical analyses means that it is impossible to perfectly match the two together. We mean to say that the HVMI, as a whole, have periodically higher depositional energies related to the LVMI. We have updated the revised manuscript to clarify this.

Page 17, line 17 – you imply that both the LVMI and HVMI units (“the studied section”) are similar to what you see in the Baltic Sea. Is this what you mean to say?

We mean to say that the system as a whole, i.e. periodic reoxygenation events, are similar to those observed in the Baltic Sea.

Page 17, lines 19 to 24 – you discuss the timescale and mechanism that is mostly likely controlling the change between LVMI and HVMI. What about within the HVMI? These changes must be much more rapid. Any educated guesses about what might be controlling this?

The resolution of data points within the HVMI is too low to support any statement about processes operating at these timescales. As such, a higher resolution study would be needed to ascertain these scales but would be difficult owing to the limitations of ammonite biostratigraphy.

Page 18, line 5 – What data repository will you use?

The data will be deposited in the Pangaea repository.

Spelling/Grammar:

Page 3, Line 24 – the word basins should not be capitalized Page 4, Line 1 – add the word “well” before “exposed” Page 4, line 9 – need a space between core list and (Fig. 1c) Page 7, line 25 (also on page 8, line 15) – add the word “relative” before “to UCC” Page 7, lines 29 and 30 – The value -27.0 should come before -28.8 ‰ Page 12, lines 1 to 9 – some grammar issues in this paragraph Page 12, line 32 – replace “of” with “for” (i.e., the need for caution when using Mo. . .)

Page 13, line 22 – proxies not proxy Page 16, line 14 – replace “is” with “are” and spell out Figure (e.g., in the Baltic Sea are plotted on Figure 9.). Page 16, line 23 – remove the “an” before “insight

We have made these corrections in the revised manuscript

Dynamic climate-driven controls on the deposition of the Kimmeridge Clay Formation in the Cleveland Basin, Yorkshire, UK

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15 Abstract

The Kimmeridge Clay Formation (KCF) is a laterally extensive, total organic carbon-rich succession deposited throughout Northwest Europe during the Kimmeridgian–Tithonian (Late Jurassic). ~~Here we present a petrographic and geochemical dataset for a 40 metre thick section of a well preserved drill core recovering thermally immature deposits of the KCF in the Cleveland Basin (Yorkshire, UK), covering an interval of approximately 800 kyr. The new data are discussed in the context of depositional processes, sediment source and supply, transport and dispersal mechanisms, water column redox conditions, and basin restriction.~~

20 ~~Armstrong et al. (2016)~~It has recently been postulated that an expanded Hadley Cell, with an intensified but alternating hydrological cycle, heavily influenced sedimentation and total organic carbon (TOC) enrichment, through promoting the primary productivity and organic matter burial, in the UK sectors of the Boreal Seaway. Consistent with such climate boundary conditions, petrographic observations, total organic carbon and carbonate contents, and major and trace element data presented here indicate that the KCF of the Cleveland Basin was deposited in the ~~distal part of the~~Laurasian Seaway under the influence of these conditions.

25 Depositional conditions alternated between three states that produced a distinct cyclicity in the lithological and geochemical records: lower variability mudstone intervals (LVMI) which comprise of clay-rich mudstone, and higher variability mudstone intervals (HVMI), which comprise TOC-rich sedimentation, and carbonate-rich sedimentation. The lower variability mudstone intervals dominate the studied interval but are punctuated by three ~2-4 m thick intervals of alternating TOC-rich and carbonate-rich sedimentation (HVMI). ~~(here termed higher variability mudstone intervals, HVMI)~~. During the lower variability mudstone intervals, conditions were quiescent with oxic to sub-oxic bottom water conditions. During

the higher variability mudstone intervals, highly dynamic conditions resulted in repeated switching of the redox system in a way similar to the modern deep basins of the Baltic Sea. During carbonate-rich sedimentation, oxic conditions prevailed, most likely due to elevated depositional energies at the seafloor by current/wave action. During TOC-rich sedimentation, intermittent anoxic-euxinic conditions led to an enrichment of redox sensitive/sulphide forming trace metals at the seafloor and a preservation of organic matter, and an active Mn-Fe particulate shuttle delivered redox sensitive/sulphide forming trace metals to the seafloor. In addition, based on TOC-S-Fe relationships, organic matter sulphurisation appears to have increased organic material preservation in about half of the analysed samples throughout the core, while the remaining samples were either dominated by excess Fe input into the system or experienced pyrite oxidation and sulphur loss during oxygenation events. New Hg/TOC data do not provide evidence of increased volcanism during this time, consistent with previous work. Set in the context of recent climate modelling, our study provides a comprehensive example of the dynamic climate-driven depositional and redox conditions that can control TOC and metal accumulations in the distal part of a shallow epicontinental sea, and is therefore key to understanding the formation of similar deposits throughout Earth's history.

1. Introduction

It is widely accepted that fine-grained marine sedimentary rocks preserve the most complete record of Earth's history (but see (Trabucho-Alexandre, 2015) and references therein for discussion). As such, understanding their formation is fundamental to investigating changes in climate, weathering regime, biogeochemical cycles, sedimentation, land-ocean linkages, and environmental change throughout geological time. Organic carbon-enriched mudstones are particularly pertinent to this as they represent dramatic perturbations in the carbon cycle, and might therefore be of value in predicting future environmental dynamics. Such mudstones also represent some of the most important global energy resources: petroleum source rocks. Understanding their formation is therefore of economic as well as environmental and broader scientific interest.

The Phanerozoic sedimentary record is punctuated by several instances of increased organic carbon burial, for example, the oceanic anoxic events during the early Toarcian, early Aptian, and early Albian (Jenkyns, 2010). The deposition of organic carbon-rich mudstones results from an interplay between the production and preservation of organic material as well as the dilution of organic material by ~~total organic carbon poor sediment~~other sedimentary components (e.g. (Sageman et al., 2003)). Sediment source and supply, primary production, biogeochemical cycling, water column redox conditions, and ocean connectivity have major implications for the formation of organic carbon-rich mudstones. However, the relative role of each of these processes is widely debated (Demaison and Moore, 1980; Pedersen and Calvert, 1990; Demaison et al., 1991; ~~Demaison and Moore, 1980; Katz, 2005;~~ Pedersen and Calvert, 1990; Tyson, 2001; Katz, 2005). The chemical makeup of a sedimentary succession can be used to assess these processes and reveal much about the depositional system, palaeoclimate,

and basin history during deposition (e.g. ~~(Brumsack, 2006)~~). When combined with petrographic observations, such analysis is a powerful tool with which environmental change can be determined over geological time.

A conceptual model developed for the Cretaceous (Hofmann and Wagner, 2011; Wagner et al., 2013) and further expanded to the Late Jurassic (Armstrong et al., 2016) linked the deposition of the total organic carbon-rich Kimmeridge Clay Formation (KCF) to atmospheric dynamics, specifically the shift and expansion of the orbitally modulated subtropical-tropical Hadley Cell, and associated changes in precipitation. Based on data from the type successions in Dorset, UK, Armstrong et al. (2016) proposed that organic carbon-lean mudstones in the Kimmeridge Clay Formation were deposited during drier intervals, characterised by mixed-layer oxygenated conditions, whereas organic carbon-rich intervals were deposited under monsoonal conditions similar to those seen in the present-day tropics. During such intervals, enhanced fresh water and nutrient input from continental runoff produced stratified basins across the Boreal Seaway (Armstrong et al. 2016). The chronostratigraphic framework indicated that major fluctuations between wet and dry conditions occurred on a short eccentricity (100 kyr) timescale (~~Armstrong et al., 2016~~; Huang et al., 2010; Armstrong et al., 2016).

Here we present total organic carbon (TOC), total sulphur (TS), carbonate, major and trace element contents, and carbon isotope data, together with petrographic observations, for the Ebberston 87 Core (Fig. 1a) in order to investigate the primary controls on Late Jurassic sedimentation and TOC enrichment in the Cleveland Basin (Yorkshire, UK); and to further refine the hypotheses proposed by Armstrong et al. (2016).

2. Geological setting

Deposited during the Kimmeridgian and Tithonian stages of the Late Jurassic, the Kimmeridge Clay Formation (KCF) is up to 620 m thick and is biostratigraphically and geochemically correlated across Northwest Europe. In the Late Jurassic, atmospheric carbon dioxide concentrations were more than four times greater than those of the present day (Sellwood and Valdes, 2008). Much of nNorthwest Europe was submerged by a shallow epicontinental sea, the Laurasian Seaway. The Laurasian Seaway comprised a series of interconnected basins, one of which was the Cleveland Basin, formed as a result of differential subsidence that started in the Triassic and continued through the Jurassic and Cretaceous (Rawson et al., 2000). The seaway connected the Boreal Sea to the Tethys Ocean through the Viking Corridor, situated between ~35 and ~40° N palaeo-latitude (Korte et al., 2015)(Fig. 1b).

Recent palaeoclimate modelling, paired with geochemistry and sedimentology from the Dorset and Yorkshire bBasins, indicates that the Laurasian Seaway was affected by a hot, humid climate comparable to present-day tropical monsoon regions (Armstrong et al., 2016). Deposition under these conditions was posited to have been strongly influenced by an intensified hydrological cycle and associated storm events. This would have promoted organic carbon enrichment through enhanced primary productivity -nutrient supply from increased precipitation and continental runoff drive nutrient supply, ocean overturn, and enhanced OM preservation from salinity/temperature stratification; and ~~redox conditions~~reduction in

bottom water ventilation. However, water depth reconstruction for the Laurasian Seaway are contentious and depend upon the preferred depositional model (Bradshaw et al., 1992). A water depth of tens of metres has been proposed by some authors (e.g. Hallam, 1975; Aigner, 1980; Oschmann, 1988), ~~— and —~~ while others (e.g. Gallois, 1976; Haq et al., 1988; Herbin et al., 1991) ~~— and —~~ have suggested a major Late Jurassic transgression that led to water depths of hundreds of metres. Reconstructions of sea-level change do not correlate with cycles in organic matter content indicating sea-level is not a primary control on organic matter enrichment (Herbin et al., 1993; Williams et al., 2001).

The KCF type section is exceptionally well-exposed along the coast around Kimmeridge Bay (~~—~~Dorset, UK; ~~—~~Fig. 1b) and was cored as part of a high-resolution analysis project (see e.g. ~~(Morgans-Bell et al., 2001)~~). It has been extensively studied by sedimentologists (Macquaker and Gawthorpe, 1993; Macquaker et al., 2010), stratigraphers (Morgans-Bell et al., 2001), palaeontologists (Lees et al., 2004), geochemists (Pearce et al., 2010), and palaeoclimatologists (Hesselbo et al., 2009) all trying to unravel the processes responsible for its deposition.

Owing to a lack of coastal outcrops, however, study of laterally equivalent deposits in the Cleveland Basin (Yorkshire, UK) has been limited to four cores drilled in the 1980s (Herbin et al., 1991; Herbin et al., 1993; Herbin and Geysant, 1993; Tribovillard et al., 1994; Boussafir et al., 1995; Herbin et al., 1995; Boussafir and Lallier-Vergès, 1997; Herbin et al., 1995; Herbin and Geysant, 1993; Herbin et al., 1991; Herbin et al., 1993; Lallier-Vergès et al., 1997; Tribovillard et al., 2004; Tribovillard et al., 1994). These four cores (Marton 87, Flixton 87, Ebberston 87, and Reighton 87; ~~—~~Fig. 1c) have been correlated to the type section in Dorset using the so-called ‘Organic Rich Bands’ (ORBs) (See ~~Fig. 6~~Fig. 6 in Armstrong et al., 2016) defined by Gallois (1979) and later referred to by Herbin and Geysant (1993).

The focus of the present study is the Ebberston 87 Ceore (54°12'47.7"N 0°37'22.7"W)~~(Herbin et al., 1991)~~, which is thermally immature (average Tmax = 425 degrees C; Herbin et al. ~~(1993)~~), and contains type II and III kerogens (Herbin et al., 1993; Scotchman, 1991). The interval of detailed analysis spans the *Pectinatites wheatleyensis* to *Pectinatites pectinatus* ammonite biozones and is equivalent to the ORBs 4 and 5 of Herbin and Geysant (1993) (Fig. 1a).

3. Materials and methods

A total of 116 samples were collected from the Ebberston 87 Ceore, stored in the IFP Energies Nouvelles (IFPEN) facilities, ~~(Chartres, France)~~. Samples of 1 cm thickness were collected at 50 cm intervals through a ~~40-metre-thick~~40-metre-thick section of the core. Sampling resolution was increased to 10 cm in darker, more organic carbon-rich intervals. Using established chronology of the Ebberston 87 Ceore (Herbin et al., 1993), and assuming a linear sedimentation rate, the studied interval spans approximately 800 kyr.

A total of 47 samples were prepared as thin sections and examined under optical light and a Scanning Electron Microscope (SEM). Samples were divided into microlithofacies based on composition, texture, and bedding features, following the nomenclature guidelines set out by Lazar et al. (2015), whereby sand is defined as any grain between 62.5 µm and 2000 µm.

coarse mud is between 62.5 μm and 32 μm , medium mud is between 32 μm and 8 μm and fine mud is anything less than 8 μm .- Grain size was measured using the rule in the SEM Aztec Software.

Total organic carbon (TOC) and total carbon (TC) were measured by LECO combustion analysis at Newcastle University. Equivalent CaCO_3 contents were calculated as $\text{CaCO}_3 = (\text{TC}-\text{TOC}) * \text{Molar Mass CaCO}_3 / \text{Molar Mass C} = (\text{TC}-\text{TOC}) * 8.33$.

- 5 Wavelength-Dispersive X-Ray Fluorescence (XRF) analyses were conducted at the Institute for Chemistry and Biology of the Marine Environment (ICBM, University of Oldenburg) to determine major (Si, Ti, Al, Fe, Mg, Ca, Na, K, P, S) -and trace (Mn, As, Ba, Ce, Co, Cr, Cu, Ga, Mo, Ni, Nb, Pb, Rb, Sr, Th, Y, V, U, Zn, and Zr) element contents of all samples. - 114 samples were decalcified with 5 % HCl to remove the carbonate and analysed for $\delta^{13}\text{C}_{\text{org}}$ values (calculated to the VPDB standard) using a Costech ECS4010 Elemental Analyzer connected to a VG TripleTrap and Optima dual-inlet mass
- 10 spectrometer -using within-run laboratory standards calibrated against NBS18, NBS-19 and NBS 22 at the- BGS stable isotope facility (part of the National Environmental Isotope Facility).BGS NERC Isotope Facility. Precision of $\pm <0.1\%$ (1 SD) was recorded. 49 samples were analysed for select trace elements (Mo, Cd, U, V, Re, Tl, As, and Sb) and Hg contents by Quadrupole Inductively Coupled Plasma Mass Spectrometry and a direct mercury analyser (DMA80, Milestone), respectively, at the Leibniz Institute for Baltic Sea Research (IOW). Major and trace elements are expressed as wt %, ppm,
- 15 and ppb, as appropriate. See supplement A for details on sample preparation and analytical procedures.

Major and trace element contents were normalised to Al to allow for assessment of relative changes irrespective of dilution by organic matter or carbonate. Aluminium was chosen as representative of the siliciclastic fine-grained sediment fraction due to its generally high contents in the samples and its limited involvement in biological, redox and diagenetic processes (Tribouillard et al., 2006). Element/Al ratios are expressed as wt%/wt%, ppm/wt%, or ppb/% as appropriate. Trace element

20 enrichment factors (EFs; Brumsack, 2006) were calculated relative to element/Al ratio of Upper Continental Crust (UCC; Rudnick and Gao, 2003).

Linear sedimentation rates (LSRs) were calculated for the *P. wheatleyensis*, *P. hudlestoni*, and *P. pectinatus* biozones using ammonite zonal boundary dates in the Geologic Timescale (Gradstein et al. 2012).

~~On geological timescales, mercury is released in large volumes during volcanism (Percival et al., 2015). A relatively long atmospheric residence time (1-2 years) means it can be globally distributed prior to deposition in the sedimentary record. Mercury enters the ocean primarily through precipitation, once in the ocean it is preferentially adsorbed on to organic matter. Assuming the Hg is adsorbed to the organic material, assessment of Hg/TOC ratios can indicate an increased/reduced supply of Hg in the system (Percival et al., 2015), hence it can be utilised as a proxy for volcanism. However, caution must be taken when interpreting records of Hg enrichments in sedimentary rocks because Hg can accumulate as a result of several other~~

25 ~~processes (e.g. Them et al. (2019)).~~

30

4. Results

Based on integrated geochemical data and petrographic observations, the studied section is divided into four lower variability mudstone intervals (LVWMI) and three distinct higher variability mudstone intervals (HVMI) at 37–40 m, 45–47 m, and 65–69 m core depth (Fig. 2). The HVMI are defined by distinct alternating facies along with repeated extreme enrichments of total organic carbon contents and trace elements, as shown on Figure 2. The *P. wheatleyensis*, *P. hudlestoni*, and *P. pectinatus* zones have LSRs of 6.6, 5.1, and 4.1 cm/ky, respectively.

4.1 Petrographic characterization

We defined six lithofacies based on compositional and textural observations (Fig. 3): 1) clastic detritus-rich medium-grained mudstone, 2) organic material and calcareous pellet-rich laminated medium to coarse-grained mudstone, 3) coccolith-dominated medium mudstone, 4) agglutinated foraminifera-bearing, medium to coarse-grained carbonaceous mudstone, 5) biogenic detritus-dominated fine to medium-grained mudstone, and 6) carbonate-cemented coarse-grained mudstone. The lower variability mudstone intervals are comprised of facies 1, 5 and 6, while the higher variability mudstone intervals are dominated by facies 2, 3, 4, and 5.

4.1.1 Lower variability mudstone interval (LVMI) petrography

Facies 1 comprises an argillaceous matrix containing medium to coarse mud-sized grains (Fig. 3). The coarsest grain fraction is fine to coarse mud-sized, unrounded quartz grains, occasional medium mud-sized chlorite grains, fine mud-sized titanium oxide grains, and very occasional phosphatic clasts. Equant pieces of organic matter (2–5 µm in diameter) and framboidal pyrite are finely disseminated throughout the matrix. Occasional organo-minerallic aggregates, comprised of wispy orange organic material (OM) and clay material, are found within the matrix. Calcitic microfossils, predominantly foraminifera tests and disarticulated shell fragments, are present, and commonly infilled with authigenic kaolinite. These mudstones have a churned texture so most of the primary sedimentary structures have been destroyed; however, some samples contain infilled burrows indicating the sediment was bioturbated (Fig. 4a). Physical mixing processes, indicated by occasional erosional surfaces, probably contributed the homogenisation of the sediment (Fig. 4b).

Facies 4 is very similar to Facies 1 but contains sand-sized quartz and is dominated by disarticulated calcitic shells, some of which are wholly or partially replaced by pyrite (Fig. 3).

Facies 6 is a medium to coarse mud-sized, angular, diagenetic carbonate grain-dominated sedimentary rock with an argillaceous matrix. Carbonate grains are microcrystalline, zoned, non-ferroan calcite and non-ferroan dolomite crystals. Relicts of the primary matrix, comprised of coccolith debris, organic matter, illitic clay and fine quartz grains, can be seen between the diagenetic components. The three samples representing this facies type (Fig. 2, three arrows in CaCO₃ plot) are

not included in the palaeoenvironmental interpretation as their primary sedimentary and geochemical signature appears to be strongly overprinted by diagenesis.

4.1.2 Higher variability mudstone interval (HVMI) petrography

Facies 2 comprises sub-mm length, discontinuous, wavy lamina organized into normally graded centimetre scale beds with erosional bases. The facies is dominated by amorphous algal marine-derived organic material aligning with and wrapped around the other sedimentary components, including the clay matrix, quartz grains, microfossils, lithic clasts, coccoliths and framboidal pyrite (Fig. 3). The ~~amorphous~~ algal ~~material-maceral~~ commonly ~~occurs-exist within~~ organo-minerallic aggregates, and extensive 'network' structures that are 500 µm thick and up to 2mm in length point towards algal mat deposition (Fig. 4c,d). Coccoliths commonly occur within faecal pellets but also in the matrix (yellow arrows in Fig. 4c,d).

Facies 3 comprises normally-graded, sub-mm laminae with erosional bases. The predominant sedimentary components are coccolith-rich faecal pellets that range in size from 30–3000 µm, unlike Facies 2 where Type II OM is a main sedimentary component (Fig. 3). The matrix is predominately pristine coccoliths and coccospheres but also contains clay minerals, equant lumps of organic material, and wispy algal macerals, calcispheres, chlorite grains, coarse mud-sized sub-rounded quartz grains, pyrite framboids (Fig. 4e), euhedral pyrite crystals (Fig. 4e), ~~and~~ occasional agglutinated foraminifera (Fig. 3), some of which are infilled with authigenic kaolinite (Fig. 4f).

Facies 5 is similar to ~~F~~facies 2 in that it has a carbonaceous, calcareous, and argillaceous matrix with medium to coarse mud-size grains. However, abundant agglutinated foraminifera, composed of quartz grains, clay minerals, and pyrite crystals, are observed in this facies. It is homogenised due to a combination of extensive bioturbation indicated by burrows and physical mixing suggested by occasional relict lamina.

4.2 Geochemistry

~~Figure 4~~Figure 5 shows a ternary diagram with the main inorganic lithogenic components represented by key proxy elements (Brumsack, 1989): clay is denoted by Al₂O₃, quartz by SiO₂, and carbonate by CaO. All samples fall on or very close to a mixing line between the calcium carbonate end member and a quartz-clay mixture that is more clay-rich than average shale (Wedepohl, 1971; Wedepohl, 1991) but less clay-rich than Upper Continental Crust (Rudnick and Gao, 2003).

Across the studied core section, total organic carbon (TOC) contents range from 0.8 wt % to 21.8 wt % with a mean of 6.6 wt %. Equivalent CaCO₃ contents range between 0.5 wt % and 73.8 wt % with a mean value of 28.5 wt % (Fig. 2). The CaCO₃ contents of three samples (51.0 m, 53.3 m, and 57.0 m; indicated by arrows in Fig. 2) are likely to be erroneous given the abundance of dolomite identified in the petrographic analysis (Fig. 3). ~~However,~~ ~~P~~petrographic and geochemical characteristics indicate strong overprinting by later-stage diagenesis (Facies 6; Fig. 3) so these samples are discounted from palaeoenvironmental interpretation.

4.2.1 Lower variability mudstone interval (LVMI) geochemistry

The lower variability mudstone intervals are characterised by TOC contents ranging from 0.8 wt % to 10.4 wt % (Fig. 2) with a mean of 4.0 wt %. ~~Marine organic matter (OM) has a higher $\delta^{13}\text{C}_{\text{org}}$ than terrestrial OM. $\delta^{13}\text{C}_{\text{org}}$ ranges from -25.7‰ to -27.9‰ with a mean of -26.7‰ (Fig. 2). Fluctuations in $\delta^{13}\text{C}_{\text{org}}$ correspond to the changes in dominant OM source (marine versus terrestrial) as demonstrated in the petrography; therefore we use $\delta^{13}\text{C}_{\text{org}}$ as a proxy for OM source.~~

Silicon and Al range between 6.1 and 22.2 wt %, and between 3.1 and 10.4 wt %, respectively. The Al-normalised ratios of Si, Ti, and Zr (indicative of coarse grain sizes and/or heavy minerals; (Dellwig et al., 2000)) range from 2.0 to 2.6, 0.04 to 0.05, and 9.8 to 17.6, respectively (Fig. 5 Fig. 6). All redox sensitive/sulphide forming trace metals (Mo, U, V, Re, Tl, As, Sb, Hg, Fe, and Mn; Fig. 6 Fig. 7, Cu, Zn, Cd; Fig. B1) are consistently lower in the LVMI compared to the HVMI. Enrichment factors (Fig. C1) calculated relative to UCC for Mo, Re, Tl, As, Sb, Hg, Cu, Zn, and Cd are generally around 1 for the LVMI. Uranium and V are slightly greater than 1 indicating a slight enrichment relative to UCC.

4.2.2 Higher variability mudstone interval (HVMI) geochemistry

In the three higher variability mudstone intervals (HVMI), TOC ranges from 2.8 wt % to 25.7 wt % with a mean of 11.7 wt %. Calcium carbonate contents range from 6.8 wt % to 88.3 wt %, and a mean of 36.0 wt %. $\delta^{13}\text{C}_{\text{org}}$ ranges from -27.0‰ to -21.8‰ , ~~to -27.0‰~~ , and the average of -25.3‰ is higher than in the lower variability mudstone intervals (Fig. 2).

The records of Si and Al exhibit larger ranges in the HVMI than in the LVMI and range from 1.9 to 23.9 wt %, and from 0.59 to 10.3 wt %, respectively. The coarse grain size/heavy mineral bound elements are slightly higher than in the LVMI. Si/Al, Ti/Al, and Zr/Al range from 2.0 to 3.3, 0.04 to 0.06, and 10.6 to 26.7, respectively (Fig. 5 Fig. 6). Silica is positively correlated with Al ($R^2 = 0.98$), which suggests that the Si is strongly associated with the clay fraction rather than biogenic, volcanogenic or diagenetic silica in the sediment, consistent with petrographic observations. We can therefore use Si/Al in conjunction with Ti/Al and Zr/Al ratios as proxies for variations in grain size, and thus depositional energy (Tribouillard et al., 2006). The grain size indicators presented here (Fig. 5 Fig. 6) suggest the HVMI are slightly coarser-grained and more variable than the LVMI. However, for samples with Al value close to 0, this could partly be an artefact of normalisation to Al, as some values in the HVMI are low in Al contents compared to the LVMI, probably due to the increased dilution of background terrigenous input by organic material and biogenic carbonate (Fig. 5 Fig. 6). Therefore, normalisation to Al in these intervals may produce spuriously high grain size proxy results and should be regarded with caution (For further discussion see (Van der Weijden, 2002) ~~for further discussion~~).

All redox-sensitive/sulphide-forming trace metals (Mo, U, V, Re, Tl, As, Sb, Hg, Fe, and Mn; Fig. 6 Fig. 7, Cu, Zn, Cd; Fig. B1) are variable and enriched relative to the LVMI. Notably, Mn/Al correlates with CaCO_3 content for the HVMI (Fig. C1). Enrichment factors (Fig. D1) calculated relative to UCC for Mo, U, V, Re, Tl, As, Sb, Cu, Zn, and Cd are variable but generally > 1 in the HVMI, indicating their enrichment relative to UCC.

5. Discussion

5.1 Productivity and organic matter composition

Biological components (coccolithophores, foraminiferans, and organic matter (OM)) occur in differing proportions throughout the section (Figs. 2 and 3). Our petrographic observations (Figs. 3 and 4) and organic carbon isotope data (Fig. 2) indicate a mixed OM type II-III component, in agreement with the published RockEval data that determines a Type II-III OM source (Herbin et al., 1993; Scotchman, 1991). Type II OM constitutes marine OM such as algal macerals, and has a higher $\delta^{13}\text{C}_{\text{org}}$ than Type III OM, which is terrigenous (Leng and Lewis, 2017). Fluctuations in $\delta^{13}\text{C}_{\text{org}}$ correspond to the changes in dominant OM source (marine versus terrestrial) as demonstrated in the petrography; therefore, we use $\delta^{13}\text{C}_{\text{org}}$ as a proxy for OM source.

5.1.1 Productivity and organic matter composition in the lower variability mudstone intervals (LVMI)

Type III OM, with typical carbon isotopes values of -26 to -28 ‰ VPDB, is ubiquitous in the LVMI (Figs. 2, 3, and 4). The OM was produced on adjacent land masses and was transported into the marine environment along with other detrital components, such as quartz and clay minerals. The largely very fine-grained nature of the LVMI suggests that organic material, together with clay-sized siliciclastic detritus, was preferentially deposited away from a major coarse-grained river system. Furthermore, Type III organic material is more resistant to oxidative degradation and hydrodynamic disaggregation due to its structure and chemistry, which explains how organic material enrichment in the LVMI (average TOC = 4.0 wt %) is possible in an environment that had an active benthic ecosystem indicative of oxic-suboxic bottom water conditions. In addition to abundant terrestrial organic material, there are occasional algal macerals in the LVMI.

5.1.2 Productivity and organic matter composition in the higher variability mudstone intervals

In contrast to the LVMI, the TOC-rich intervals of the HVMI (average TOC = 12.3 wt %) are dominated by Type II OM. Wispy lamina, algal maceral material (Figs. 3 and 4), and algal mats are the main source of OM in these intervals, although Type III OM remains ubiquitous and coincides with the occurrence of detrital material, i.e. quartz grains, lithic clasts, and clay minerals in the samples. In the TOC-rich parts of the HVMI, large amounts of type II algal derived material deposited at the seafloor acted to dilute the detrital sediment and type III OM.

The occurrence of organo-mineralic aggregates and algal OM (20 μm thick and 200 μm long; Fig. 3) demonstrate marine snow and algal mat settling as key mechanisms for the delivery of OM to the seafloor (Macquaker et al., 2010). Filter-feeding organisms strip nutrients and fine grained sediment out of the water column and excrete them as faecal pellets (Ittekkot et al., 1992). This biological mediation of the sediment is a key process in the export of OM, sediment, and nutrients from the water column to the sediment. Ittekkot et al. (1992) demonstrated a link between enhanced sediment and nutrient flux to the ocean during wet phases of the monsoonal cycle. They showed also that there was an increase in biotic-

abiotic pellet production, and thus an enhanced OM and mineral flux to the seafloor, in response to enhanced continental runoff and weathering associated with the monsoonal wet phases.

Production of algal macerals in the oceans is affected by the availability of light and nutrients (Pedersen and Calvert, 1990). Given the palaeolatitudinal positioning of the section (Fig. 1b) it is likely that light did not limit primary productivity. We therefore propose that nutrient availability was the driver of changes in productivity. Nutrients are supplied to the euphotic zone through continental weathering or upwelling/overturning of nutrient rich waters. Given the palaeogeographic setting of the Cleveland Basin in an epicontinental seaway, it is likely that changes in precipitation on the surrounding landmasses were a key driver of changes in productivity. The wet-dry cycles proposed by recent climate modelling (Armstrong et al., 2016) may therefore be the key driver behind oscillations in the production and preservation of TOC, i.e. the switching between the LVMI's and HVMI's. Alternatively, the variations in TOC could result from variable dilution of the OM by carbonate or detrital material, or the variations could result from a combination of both dilution and wet-dry cycles.

Carbonate productivity, mainly in the form of coccoliths, varies throughout the studied KCF section and is at its maximum within the carbonate-rich sections of the HVMI's. High nutrient availability in the photic zone of the water column, indicated by high OM productivity, also influences the rate of carbonate productivity (Lees et al., 2006). Within the HVMI's, alternations between TOC-rich deposition likely occurred during high nutrient availability, and carbonate-rich deposition is more likely under less nutrient-rich conditions. This alternation may result from ecological switching driven by oceanographic or climate processes that subtly altered the nutrient levels during these intervals. The organisation of the coccoliths into faecal pellets in both the TOC-rich and carbonate-rich intervals of the HVMI's indicates a high abundance of higher trophic organisms to graze on a plentiful supply of food further supporting an elevated nutrient level during these intervals. Furthermore, faecal pellets reduce the time taken for sediment to reach the seafloor (e.g. Shanks, 2002) so the abundance of pellets and organo-mineralic aggregates led to increased OM export efficiency thus enhanced OM preservation (Macquaker et al., 2010). For the Dorset section, Macquaker et al. (2010) suggested that zooplankton were the main grazers and producers of faecal pellets. Our petrographic study of the Ebberston 87 Core reveals strong similarities with the type section in Dorset, so we tentatively suggest that zooplankton were also the main grazers in the Cleveland Basin at the time of deposition. Alternatively, variations in carbonate may be as a result of dilution by other sedimentary components. ~~In contrast, the HVMI's contain marine organic material and carbonate rich faecal pellets. The occurrence of organo mineral aggregates and algal OM (20 µm thick and 200 µm long; Fig. 3) demonstrate marine snow and algal mat settling as key mechanisms for the delivery of OM to the seafloor (Macquaker et al., 2010). Filter feeding organisms strip nutrients and fine grained sediment out of the water column and excrete them as faecal pellets (Ittekkot et al., 1992). This biological mediation of the sediment is a key process in the export of OM, sediment, and nutrients from the water column to the sediment. Ittekkot et al. (1992) demonstrated a link between enhanced sediment and nutrient flux to the ocean during wet phases of the monsoonal cycle. They showed also that there was an increase in biotic abiotic pellet production, and thus an~~

enhanced OM and mineral flux to the seafloor, in response to enhanced continental runoff and weathering associated with the monsoonal wet phases.

5.21 Depositional environment: sediment source, depositional energy, dispersal mechanisms, and climatic context

The studied succession is a three-component system, comprising clay-dominated, organic carbon-dominated, and carbonate-dominated facies (Fig. 3). The clay fraction of the mudstones is probably derived from detrital inputs to the basin, through the weathering of nearby emergent landmasses. Possible sources include Cornubia, or the Welsh, Irish, or London-Brabant landmasses (Fig. 1b), as discussed by Hesselbo et al. (2009). Terrestrial organic matter (OM) was likely washed into the basin along with detrital clays, while carbonate and marine OM formed in the water column.

On geological timescales, mercury is released in large volumes during volcanism (Percival et al., 2015). A relatively long atmospheric residence time (1-2 years) means it can be globally distributed prior to deposition in the sedimentary record. Mercury enters the ocean primarily through precipitation, once in the ocean it is preferentially adsorbed on to organic matter. Assuming the Hg is adsorbed to the organic material, assessment of Hg/TOC ratios can indicate an increased/reduced supply of Hg in the system (Percival et al., 2015), hence it can be utilised as a proxy for volcanism. However, caution must be taken when interpreting records of Hg enrichments in sedimentary rocks because Hg can accumulate as a result of several other

processes (e.g. (Them et al., 2019; Grasby et al., 2019)). Diagenesis may affect Hg contents, depending upon which sedimentary component hosts the it (e.g. organic matter or pyrite), ongoing research is still exploring this (Them et al., 2019). A volcanogenic sediment source is ruled out using Hg/TOC as a proxy (Scaife et al., 2017)(~~Fig. 5~~Fig. 6), which agrees with other studies of the KCF (Percival et al., 2015), and petrographic evidence (conchoidally fractured quartz grains without Fe oxide rims) rules out an aeolian source, which is also supported by the palaeogeographical position of this basin in the outer palaeo-subtropics (Armstrong et al., 2016).

The SiO₂, Al₂O₃, and CaCO₃ ternary diagram (Fig. 53) suggests the studied mudstones have an overall finer grain size than average shale. This may result from either the presence of more clay material or a higher contribution of Al-rich clay minerals (e.g., kaolinite), however petrographic results show a predominance of illite (K-Al rich clay mineral) in the matrix suggesting it is more clay-rich than average shale, which corroborates published XRD analyses (Herbin et al., 1991). The fine grained nature of the sedimentary rock may indicate a siliciclastic starvation process. In this, It is possible that either the coarse-grained siliciclastic fraction of the sediment was trapped in nearshore proximal settings, with only fine-grained material being transported to more distal settings within the Cleveland Basin. Alternatively, or that, the fine-grained nature of the sediment may result from the weathering of fine-grained source material on the hinterland or the deposition of palimpsest sediment that was deposited and remobilised on the ocean. Nevertheless, linear sedimentation rates (LSRs) were calculated of 6.6, 5.1, and 4.1 cm/ky for the *P. wheatleyensis*, *P. hudlestoni*, and *P. pectinatus* ammonite biozones, respectively, indicate the system was not starved of sediment.

Depth plots of geochemical grain size proxies (Fig. 5 Fig. 6) indicate generally quiescent conditions in the LVMI, with slightly more variable energy in the HVMI. Petrographic observations support the geochemical grain size proxies, showing a lower proportion of clay material and a dominance of alternating organic carbon- and carbonate-rich sediment in the HVMI (particularly in facies 2 and 3). In addition to the compositional variations, the occurrence of normally-graded beds with erosional bases in TOC-rich sections of the HVMI indicates an energetically dynamic setting. Occasional higher energy conditions affected sediment deposition and dispersal at the seafloor and led to winnowing of the finest grain sizes. Significant quantities of terrestrial OM (identified by $\delta^{13}\text{C}_{\text{org}}$ and petrography), coupled with its overall fine-grained nature, suggest that the sediments accumulated in a distal depositional setting where hydrodynamic processes sorted the sediment based on particle size and density.

Owing to the shallow gradients and vast extent of epicontinental seaways, sediment dispersal in the LVMI, which are dominated by terrigenous mud, is likely to have been controlled by wind- and tide-induced bottom currents (Schieber, 2016); however, uncertainty on water depths in the Cleveland Basin at the time of deposition means it is not possible to determine the significance of these processes. In contrast, the HVMI contain marine organic material and carbonate rich faecal pellets. The occurrence of organo-mineral aggregates and algal OM (20 μm thick and 200 μm long; Fig. 3) demonstrate marine snow and algal mat settling as key mechanisms for the delivery of OM to the seafloor (Macquaker et al., 2010). Filter-feeding organisms strip nutrients and fine grained sediment out of the water column and excrete them as faecal pellets (Ittekkot et al., 1992). This biological mediation of the sediment is a key process in the export of OM, sediment, and nutrients from the water column to the sediment. Ittekkot et al. (1992) demonstrated a link between enhanced sediment and nutrient flux to the ocean during wet phases of the monsoonal cycle. They showed also that there was an increase in biotic-abiotic pellet production, and thus an enhanced OM and mineral flux to the seafloor, in response to enhanced continental runoff and weathering associated with the monsoonal wet phases.

The occurrence of faecal pellets, increases in grain size, TOC, and CaCO_3 observed in the HVMI studied here points towards enhanced productivity, which is likely to be a regional phenomenon. If this was not limited to the Cleveland Basin, it may explain a coeval organic enrichment across the Laurasian Seaway. The causal mechanism behind the increase in productivity cannot be constrained with the present dataset. However, slight increases in depositional energy may result from intermittent storm mixing or changes in bottom water currents, which could both increase primary productivity.

Armstrong et al. (2016) attributed alternations in TOC enrichment to orbitally forced changes in humidity-aridity occurring over a short eccentricity timescale (100 kyr). Based on the chronostratigraphic time frame for the Yorkshire and Dorset sections (Armstrong et al., 2016; Huang et al., 2010) and assuming a linear sedimentation rate, the changes between the HVMI and LVMI equate with short eccentricity cycles. Thus our observations match with the prediction of Armstrong et al. (2016) that enhanced TOC burial occurred during wet periods through enhanced continental weathering, nutrient supply to the ocean, and primary productivity. The astrochronological timescale established for the Swanworth Quarry 1 Core in the Wessex Basin (Huang et al., 2010) and applied to the Ebberston 87 Core in the Cleveland Basin (Armstrong et al., 2016) is

plotted for references in Fig.1a. Given the relatively short duration of the studied interval, it is not possible to conduct further spectral analysis with the present dataset.

5.2 Productivity and organic matter composition

Biological components (coenocolithophores, foraminiferans, and organic carbon) occur in differing proportions throughout the section (Figs. 2 and 3). Our petrographic observations (Fig. 2) and organic carbon isotope data (Fig. 3) indicate a mixed OM type II-III component, in agreement with the literature (Herbin et al., 1993; Scotchman, 1991). Marine organic matter (OM) has a higher $\delta^{13}\text{C}_{\text{org}}$ than terrestrial OM. Fluctuations in $\delta^{13}\text{C}_{\text{org}}$ correspond to the changes in dominant OM source (marine versus terrestrial) as demonstrated in the petrography; therefore we use $\delta^{13}\text{C}_{\text{org}}$ as a proxy for OM source. Type III OM, with typical carbon isotopes values of -26 to -28 ‰ VPDB, is ubiquitous in the LVMI (Figs. 2 and 3). The OM was produced on adjacent land masses and was transported into the marine environment along with other detrital components, such as quartz and clay minerals. The largely very fine grained nature of the LVMI suggests that organic material, together with clay sized siliciclastic detritus, was preferentially deposited in the distal location represented by the Ebberston core. Furthermore, Type III organic material is more resistant to oxidative degradation and hydrodynamic disaggregation due to its structure and chemistry, which explains how organic material enrichment in the LVMI (average TOC = 4.0 wt %) is possible in an environment that had an active benthic ecosystem indicative of oxic-suboxic bottom water conditions. In addition to abundant terrestrial organic material, there are occasional algal macerals in the LVMI.

In contrast, the TOC rich intervals of the HVMI (average TOC = 12.3 wt %) are dominated by Type II OM. Wispy lamina, algal maceral material (Fig. 3), and algal mats are the main source of OM in these intervals, although Type III OM remains ubiquitous and coincides with the occurrence of detrital material, i.e. quartz grains, lithic clasts, and clay minerals in the samples. In the TOC rich parts of the HVMI, large amounts of type II algal derived material deposited at the seafloor acted to dilute the detrital sediment and type III OM.

Production of algal macerals in the oceans is affected by the availability of light and nutrients (Pedersen and Calvert, 1990). Water depth is not likely to have exceeded a few hundreds of meters in the distal Cleveland Basin (Bradshaw et al., 1992), suggesting that the euphotic zone could have reached the seafloor and light did not limit primary productivity. We therefore propose that nutrient availability was the likely driver of changes in productivity. Nutrients are supplied to the euphotic zone through continental weathering or upwelling/overturning of nutrient rich waters. Given the palaeogeographic setting of the Cleveland Basin in an epicontinental seaway, it is likely that changes in precipitation on the surrounding landmasses were a key driver of changes in productivity. The wet-dry cycles proposed by recent climate modelling (Armstrong et al., 2016) may therefore be the key driver behind oscillations in the production and preservation of TOC, i.e. the switching between the LVMI and HVMI.

Carbonate productivity, mainly in the form of coenocoliths, varies throughout the studied KCF section and is at its maximum within the carbonate rich sections of the HVMI. High nutrient availability in the photic zone of the water column, indicated

by high OM productivity, also influences the rate of carbonate productivity (Lees et al., 2006). Within the HVMI's, alternations between TOC rich deposition likely occurred during high nutrient availability, and carbonate rich deposition is more likely under less nutrient rich conditions. This alternation may result from ecological switching driven by oceanographic or climate processes that subtly altered the nutrient levels during these intervals. The organisation of the coccoliths into faecal pellets in both the TOC rich and carbonate rich intervals of the HVMI's indicates a high abundance of higher trophic organisms to graze on a plentiful supply of food further supporting an elevated nutrient level during these intervals. For the Dorset section, Macquaker et al. (2010) suggested that zooplankton were the main grazers and producers of faecal pellets. Our petrographic study of the Ebberston 87 core reveals strong similarities with the type section in Dorset, so we tentatively suggest that zooplankton were also the main grazers in the Cleveland Basin at the time of deposition.

5.3 Redox conditions

5.3.1 Redox conditions in the lower variability mudstone intervals (LVMI's)

In the lower variability mudstone intervals, petrographic results demonstrate extensive bioturbation, most likely resulting from widespread faunal colonisation of the sediment surface due to well-oxygenated bottom waters (Fig. 4). However, enrichment factors of redox-sensitive trace elements (Mo and U elements) (Fig. 78) (Brumsack, 2006; Tribovillard et al., 2006; Piper and Calvert, 2009) indicate that during the deposition of the LVMI's, the sediment pore water was suboxic to anoxic. This interpretation is further supported by the low Mn/Al and high (TOC=0.8–10.4 wt %; Fig. 2) TOC contents.

It is difficult to reconcile the high TOC contents, which are considered extremely TOC-rich and qualifies as a potential hydrocarbon source rock, with oxygenated bottom waters. We explain this apparent conundrum by the presence of terrestrial OM in the LVMI's as demonstrated by lower $\delta^{13}\text{C}_{\text{org}}$ (Fig. 2), petrography (Fig. 3) from this study, and from published Rock Eval data (Herbin et al., 1993). In comparison to its marine counterpart, terrestrial organic matter often has a higher preservation potential because its chemical structure can make it less susceptible to oxidative degradation and because sulphate reducing bacteria have a lower affinity for terrestrial OM (Dellwig et al., 2001). Similarly, marine algal macerals have a greater chance of being preserved when incorporated into organo-minerallic aggregates that are observed in the HVMI's, because physical and chemical attractions between the aggregate components can form a protective barrier to oxidants thus reduce oxidative destruction of the algal macerals (Macquaker et al., 2010).

5.3.2 Redox conditions in the ~~Highly Fluctuating Intervals~~ higher variability mudstone intervals (HVMI's)

The TOC-rich parts of the HVMI's are dominated by algal macerals (Figs. 3 and 4), which account for the elevated TOC concentrations of up to 25.7 wt % (Fig. 2). Enrichments in redox sensitive/sulphide forming elements (Mo, U, V, Zn, Cd, Re, As, Sb, Hg, and Fe; Fig. 6 Fig. 7, Zn and Cd; Fig. B1) clearly support the notion of periodically anoxic to euxinic pore and bottom waters at the study site (Brumsack, 2006; Tribovillard et al., 2006), which enhanced preservation of OM during these

intervals. However, the presence of agglutinated foraminifera within the TOC-rich parts of the HVMI, as well as enrichments of Mn relative to the LVMI (Fig. 6 Fig. 7), argue that oxygen must have been present at the seafloor, at least episodically (Dellwig et al., 2018; Macquaker et al., 2010). A positive correlation between Mn/Al and CaCO₃ in the HVMI (Fig. B1) is further evidence that during favourable conditions for CaCO₃ formation, Mn was sequestered into the sediment thus implying repeated oxygenation events (but see (Herndon et al., 2018) for alternative discussion). ~~But note that the enrichment factor of Mn in the HVMI is on a much lower level than for sediments of the Baltic Sea deeps (Fig. 9).~~ Nevertheless, this scenario has similarities to the modern Baltic Sea deeps (Landsort Deep, Gotland Basin) that display dramatic shifts between euxinic conditions during stagnation and oxic conditions during North Sea water incursions, leading to the sequestration of large amounts of Mn carbonate into the sediments (Dellwig et al., 2018; Häusler et al., 2018; Scholz et al., 2018).

5.3.3 Fe enrichment and sulphide formation

The significant enrichments of Fe in the TOC-rich intervals of the HVMI are related to microbial sulphate reduction and pyrite formation, following dissolution of Fe (oxyhydr)oxides at the seafloor. The formation of pyrite (FeS₂) depends on the redox conditions of the sediment pore and overlying water column, so it can be used to reconstruct palaeoenvironmental conditions beyond the redox state (Hetzl et al., 2011). ~~Figure-Figure 87~~ shows a Fe_x-TOC-S ternary diagram for the studied interval. Reactive iron is calculated as $Fe_x = Fe - 0.25 \cdot Al$ to account for the fraction of Fe that is bound in the silicate fraction and unavailable for redox reactions (Brumsack, 1988; Dellwig et al., 1999). A fully quantified measurement of reactive iron in a sample must be determined experimentally, owing to an absence of this, we discuss samples only in a relative way. For the samples plotting above the TOC-pyrite mixing line, pyrite formation was limited by the availability of sulphur (in the form of H₂S generated by bacterial sulphate reduction) and excess, less-pyritised reactive iron was preserved in the sediments (potentially as oxides or carbonates). Both in the LVMI and the HVMI, there are samples with an excess of reactive Fe relative to S. Limited availability of reactive OM to support bacterial sulphate reduction (i.e. limited H₂S generation) may be the reason for the observed excess iron. Alternatively, it might either be related to the re-oxidation of pyrite during oxygenation events (removing S but not Fe from the sediment), or a strong input of Fe into the system via a particulate shuttle mechanism (discussed in sect. 5.3.4).

The samples that plot near the TOC-pyrite mixing line in ~~Figure-Figure 87~~ are assumed to represent an availability of reactive Fe and S in the system that matches the stoichiometry of pyrite, hence they have a higher degree of pyritisation. ~~Pyritisation explains the enrichment of metals known to accumulate with pyrite (e.g., As, Sb and Mo; Depth-plots of As/Al and Sb/Al (Fig. 6), trace elements that are known to accumulate strongly in pyrite, support these conditions~~ (Tribouillard et al., 2004). In samples that plot below the TOC-pyrite mixing line in ~~Figure-Figure 87~~, pyrite formation is limited by the availability of reactive iron, meaning the degree of pyritisation was high but there also was an excess of sulphide available in the system. Under these conditions, sulphide was able to react with OM through sulphurisation (or natural vulcanisation).

Our results are consistent with (Tribovillard et al., 2004) who concluded that pyrite formation prior to OM sulphurisation may increase the sequestration of Mo into the sediment. This highlights the need ~~for~~ caution when using Mo as a single diagnostic proxy in palaeoenvironmental reconstruction. (Tribovillard et al., 2004) further demonstrated a linear relationship between the quantity of ‘orange algal macerals’ and Mo concentrations in the Ebberston 87 ~~Ceore~~, supporting the presence of sulphurised OM. The resulting sulphurised OM is less vulnerable to oxidative degradation and thus has a greater preservation potential during burial. We suggest that this mechanism is partly the reason we observe high TOC ~~concentrations~~ contents in intervals that underwent first sustained periods of pore or bottom water euxinia and later periods of reoxygenation. Studying Jurassic sediments of the Marton 87 ~~Ceore~~ (Fig. 1c), drilled 4 km away from the Ebberston 87 ~~Ceore~~, (Boussafir et al., 1995) and (Lallier-Vergès et al., 1997) also conclude that sulphurisation/natural vulcanisation of Type II OM enhanced organic material preservation potential.

5.3.4 Evidence for a Fe-Mn shuttle and ocean restriction

In the context of pyrite formation versus OM sulphurisation, and the enrichment of trace metals at the seafloor, the delivery of Fe and Mn (oxyhydr)oxides via a so-called particulate shuttle may play an important role. The particulate shuttle effect describes the cycling of Mn and Fe through the redoxcline, which is an ocean layer characterised by steep geochemical gradients, that are driven by changes, and the point at which solubility of certain mineral phases increases or diminishes, in particular Mn, Fe, and P phases (Dellwig et al., 2010). Dissolved Mn^{2+} diffuses from anoxic waters beneath the redoxcline to the oxygenated surface layer where it is oxidised to form MnO_2 particles. These particles react with Fe^{2+} to form mixed Mn/Fe (oxyhydr)oxide ~~phases~~ particulates which are highly efficient adsorbents of dissolved trace metals in the ocean (Goldberg, 1954). If these ~~phases~~ particulates sink and reach deeper sulphidic waters, the (oxyhydr)oxides are reduced, and Mn^{2+} diffuses back into the overlying waters, while Fe^{2+} reacts with H_2S to form Fe sulphides that incorporate part of the released trace metals (Canfield et al., 1992; ~~Huckriede and Meischner, 1996; Neretin et al., 2004;~~ Dellwig et al., 2010; ~~Huckriede and Meischner, 1996; Neretin et al., 2004;~~ Tribovillard et al., 2015). This particulate shuttle plays a key role in the transfer of trace elements from the water column to the sediment (Goldberg, 1954; Tribovillard et al., 2015), and is particularly effective when redox conditions fluctuate (Algeo and Tribovillard, 2009). Of particular relevance to this study is the transfer of Mo, As, and Sb to the sediment, elements that Tribovillard et al. (2015) used as proxies for the presence of a Mn-Fe shuttle in ancient anoxic-euxinic ocean basins. In the present study, Fe/Al (Fig. 6 Fig. 7) and Mo/U (Fig. 9 Fig. 9a) co-variations point towards a Mn-Fe shuttle operating during deposition of TOC-rich sediment in the HVMI. Manganese is repeatedly reduced and re-oxidised through the shuttle and does not get removed into the sediments as long as bottom water conditions are suboxic, leading to a build-up of dissolved Mn in the water column. Therefore, the Mn contents encountered in the oxic layers are easily accounted for due to fast deposition of Mn oxide from the water column and subsequent transformation into Mn carbonates within the sediments. ~~Manganese is repeatedly recycled through the shuttle so the observed concentrations are easily accounted for.~~ Peaks in Fe/Al coincide with peaks in pyrite associated trace metals (As/Al, Sb/Al;

~~Fig. 6~~Fig. 7) and increased abundance of pyrite in thin sections (Fig. 3). We propose that a suboxic shuttle that remobilised Fe from shelf sediments (Wijsman et al., 2001, Severmann et al., 2008, Dellwig et al., 2010; Eckert et al., 2013; Severmann et al., 2008; Wijsman et al., 2001) was active during deposition of the TOC-rich parts of the HVMI in the Ebberston 87 Ceore, and enriched reactive Fe in the sediments to levels significantly above UCC. Episodically high inputs of reactive Fe via a suboxic shuttle also prevented the accumulation of H₂S in the pore waters, thereby limiting OM sulphurisation. During ventilation events (as suggested by benthic foraminifera and Mn enrichments), some of the pyrite was reoxidised, and sulphate diffused from the pore water to the water column while reactive Fe was retained in the sediment by precipitation of Fe (oxyhydr)oxides. Thus, samples that appear to be deposited under S limited conditions in ~~Figure~~Figure 87 may still contain organic sulphur. We conclude that the hyper-accumulation of TOC in this setting was controlled by high primary productivity, increased OM production, the balance of H₂S generation, and the supply of reactive Fe via a suboxic shuttle.

In the context of developing an anoxic/euxinic water column in the Cleveland Basin, ~~with associated enrichments of redox sensitive/sulphide forming trace metals (Fig. 6)~~, not only primary productivity but also basin restriction has to be considered as a contributing factor. ~~A key element for the reconstruction of hydrographic basin restriction is Mo (Algeo and Lyons, 2006), as its removal from the water column and sequestration into the sediments changes dramatically under different redox conditions, more so than it is the case for other redox sensitive/sulphide forming trace metals (Helz et al., 1996).~~

Due to the specific biogeochemical behaviour of Mo, ~~the ratio of~~ Mo/U enrichment factors ~~can give~~have been shown to give insights into the degree of restriction of a basin with examples from the Carico Basin, the Black Sea, the Late Pennsylvanian Midcontinent Sea, and the Late Devonian Seaway (Algeo and ~~Lyons~~Tribovillard, 2009). Both elements tend to be enriched in sediments deposited under oxygen-depleted bottom water conditions, but to varying degrees (Helz et al., 1996). Under suboxic conditions, U enrichment is likely to exceed Mo enrichment owing to the trapping of U at the Fe(II)/Fe(III) redox boundary (Algeo and Tribovillard, 2009). As oxygenation of the water mass decreases further, and sulphidic conditions develop in pore and bottom waters, Mo enrichment increases relative to that of U, and the Mo/U ratio approaches or surpasses that of seawater due to the presence of sufficient H₂S to convert the conservative molybdate ion to the highly particle-reactive thiomolybdate (Algeo and Tribovillard, 2009; Erickson and Helz, 2000). Mo/U ratios for the LVMI in this study are similar to that of average shale (~~Fig.~~Fig. 98a), pointing towards a detrital, rather than authigenic, source of the Mo and U in these samples. Therefore, these samples cannot be used to investigate the presence of a Mn-Fe shuttle. In contrast, the HVMI display repeated peaks in the Mo/U ratio, indicative of strong Mo enrichments under euxinic conditions, facilitated by the activity of a Mn-Fe shuttle preferentially transferring Mo from the water column to the sediment (Algeo and Tribovillard, 2009).

We compare our new results with existing data from Tribovillard et al. (2004), who analysed trace elements (~~Fig.~~Fig. 9b8) in several samples from the Ebberston 87 Ceore, with cycle 3 in their study being equivalent to the stratigraphically oldest (*Pectinatites wheatleyensis*) HVMI in our study. The authors concluded that TOC enrichment in the Cleveland Basin occurred during times of transgression due to siliciclastic sediment starvation, high primary productivity, and water column

stratification. Our higher resolution sampled data agree with this conclusion in that on a Mo-U enrichment factor plot (~~Fig. Fig. 98b~~), the TOC-rich intervals plot clearly within the particulate shuttle field, ~~which is good agreement with our Fe/Al and Mn/Al data discussed above~~. Samples from the LVMIIs plot outside of this field, which confirms that during deposition of these samples the suboxic conditions were limited to the sediment. Pearce et al. (2010) concluded that the deposition of the KCF occurred in an unrestricted basin. (Tribovillard et al., 2012) compared their results to those presented by Pearce et al. (2010) and agreed that it is unlikely that either the Cleveland or Wessex Basins were restricted for a prolonged period, if at all. In combination with our geochemical and petrographic data, we can confirm that the repeated development of anoxic/euxinic conditions in the ~~distal~~ Cleveland Basin was most likely due to high primary productivity, and possibly salinity stratification due to high amounts of freshwater runoff, but it is unlikely that the Cleveland Basin experienced prolonged restriction.

5.3.5 Comparison to modern organic carbon-rich sediments

Comparing our data with those from different TOC-rich deposits enables us to better understand common processes involved in TOC enrichment in different palaeoenvironmental/depositional settings (~~Brumsack, 2006~~) and draw wider conclusions for the present study. ~~Figure 9~~ Figure 10 shows average enrichment factors (calculated with respect to average shale for select trace metals, ~~(Mn, As, Cd, Co, Cu, Mo, Re, Sb, U, V, and Zn,~~ to facilitate direct comparison with the data in Brumsack, 2006) for the carbonate-rich and TOC-rich sections of the HVMIIs in the present study and other well-studied deposits. Depositional environments, in which TOC and trace elements are enriched, can fall on a scale between two end members; coastal upwelling systems (e.g. Gulf of California, Peru coastal margin) and anoxic basin type settings (e.g. Mediterranean Sapropels, Black Sea, Baltic Sea deeps). The former are characterised by seasonally high primary productivity and extensive oxygen minimum zones (OMZ) that are fuelled by wind-driven upwelling of high nutrient and trace metal waters, while the latter are characterised by permanent salinity stratification and water mass restriction (Brumsack, 2006).

The HVMIIs in the present study bear similarities to the Gulf of California in that they exhibit similarities in Cd enrichment and ~~Mn-depleted in Mn in comparison to the HVMIIs~~ depletion, indicating high productivity and suboxic conditions in the water column (Sweere et al., 2016). Cd enrichments suggest that parts of the HVMIIs experienced upwelling like processes, which may have resulted in high productivity. However, sulphidic conditions in the water column are rarely observed in upwelling settings (Brumsack, 2006); this differs from the studied Cleveland Basin and is reflected in the sulphide indicators (As and Mo; ~~Fig. 6~~ Fig. 7). This indicates that the method of trace metal sequestration is different in modern upwelling settings and the studied section, meaning they are a poor analogue for the present study.

The anoxic basin type settings exhibit strong enrichments in sulphide forming trace metals (Brumsack, 2006). However, the enrichment factors for the Mediterranean Sapropels and Units 1 and 2 from the Black Sea exhibit different patterns (~~Fig. 9~~ Fig. 10), owing to the pronounced depletion of trace elements in the water column of the Black Sea during Unit 1 and less pronounced euxinia during most parts of Unit 2 (Wegwerth et al., 2018). The studied HVMIIs are most similar to Black Sea

Unit 2 in that redox sensitive (As, Cu, Mo, Re, U, V, and Zn) and productivity (Cd) elements are on the same order of magnitude. From this, we may infer similarities operating in Black Sea Unit II and the HVMI~~the two intervals of deposition~~. However, the modern Black Sea is permanently stratified and is governed by its unique hydrological setting. This is in stark contrast to the HVMI in the Cleveland Basin, which exhibit rapid oscillations and were deposited in a shallow epicontinental seaway. It may be that the Late Jurassic Laurasian Seaway fluctuated between a setting close to an anoxic basin type setting and setting more analogous to a coastal upwelling zone.

5.3.6 Evidence for Baltic Sea characteristics

While the studied interval shares similarities and differences with both upwelling and anoxic basin type settings, we are still lacking an appropriate modern analogue. Palaeogeography exerts a fundamental control on sedimentation, in particular, TOC enrichment, but there is no modern-day example of a shallow epicontinental seaway. See Algeo et al. (2008) for discussion of possible analogues. ~~If at all,~~ the Baltic Sea comprises a series of small basins that are interconnected by narrow sills and channels and bears resemblance to the Late Jurassic Laurasian Seaway. ~~We propose that redox dynamics in the Cleveland Basin during the Late Jurassic shared similarities to those in the modern-day Baltic Sea in that they both fluctuated between LVMI and HVMI deposition exhibit signs of complex redox dynamics and trace metal sequestration.~~ The enrichment factors in Fig. 9 Fig. 10 are averaged across the HVMI, indicating Mn depletion across these zones. However, there are several samples that are enriched in Mn within the HVMI (Fig. 6 Fig. 7), which point towards prolonged reoxygenation events during episodes of organic enrichment in the Kimmeridge Clay Formation. †

The Baltic Sea† receives saline water input from the North Sea and fresh water from riverine input resulting in permanent stratification of the water column (Dellwig et al., 2018; Häusler et al., 2018). Coupled restriction of water mass exchange in the deeper sub-basins of the Baltic Sea leads to appearance of water column anoxia/euxinia. However, large (and infrequent) inputs of saline and oxic water from the North Sea promote overturning and reoxygenation of the Baltic Sea deeps, causing extensive Mn carbonate formation in the sediments (Dellwig et al., 2018; Häusler et al., 2018). While the detailed mechanisms of Mn carbonate formation are still debated, the Mn carbonate deposits are generally associated with intervals of prolonged reoxygenation (e.g., in the Baltic Sea, plotted on Fig. 10) (Häusler et al., 2018) and most likely benefit from microbial mediation (Henkel et al. 2019). The Baltic Sea deeps represent an extreme example of Mn shuttling, where Mo is highly enriched as it adsorbed to Mn but U and Re are much less enriched. Enrichment factors calculated relative to average shale (Wedepohl, 1971; Wedepohl, 1991) for the Landsort Deep in the Baltic Sea is plotted on Fig. 9 Fig. 10. Data was generated from the 36GC-4 Ceore (see (Häusler et al., 2017; Häusler et al., 2018; Dellwig et al., 2019; Häusler et al., 2017) for Landsort Landsort Deep ceore and site description and age model) and is presented in the data repository.

~~This geographical setting bears resemblance to the Late Jurassic Laurasian Seaway in that it was comprised of a series of interconnected shallow basins. Therefore, we propose that redox dynamics in the Cleveland Basin during the Late Jurassic shared similarities to those in the modern-day Baltic Sea in that they both exhibit signs of complex redox dynamics and trace~~

~~metal sequestration. The enrichment factors in Fig. 9 are averaged across the HVMI, indicating Mn depletion across these zones. However, there are several samples that are enriched in Mn within the HVMI (Fig. 6), which point towards prolonged reoxygenation events during episodes of organic enrichment in the Kimmeridge Clay Formation.~~

6. Conclusions and conceptual model

5 This study provides ~~an~~ insight in to the sedimentation in ~~the distal parts of~~ an epicontinental seaway during a greenhouse world. Examining sediment away from strong detrital dilution and overprint allows us to unpick the global controls on sedimentation and gives us further insight in to the key processes in this palaeogeographic setting. Far away from detrital inputs, this ~~distal~~ location provides an excellent data set for examining changes in water column processes.

10 The studied interval of the Kimmeridge Clay Formation in ~~the distal part of~~ the Cleveland Basin was deposited in a highly dynamic environment that fluctuated from LVMI deposition to HVMI (Fig. ~~10~~Fig. 11). During LVMI sedimentation (Fig. ~~10~~Fig. 11a), the water column was oxic and was able to sustain life to a degree that the sediment was extensively bioturbated. However, the sediment pore waters were suboxic ~~to anoxic~~ which facilitated the enrichment of TOC.

15 During each HVMI, the depositional environment experienced episodic and drastic changes. Trace element data indicate redox conditions of the bottom waters alternating between fully oxic and euxinic. During oxic conditions, organic matter (OM) and carbonate production proliferated (10a, b). High primary productivity led to an increase in higher trophic feeders that produced masses of faecal pellets, in turn resulting in an increase in OM flux rate to the seafloor that aided the preservation of carbon and diluted the detrital material. At the same time, Mn and Fe (oxyhydr)oxides were deposited at the seafloor, together with adsorbed trace metals (Fig. ~~10~~Fig. 11b). Detrital element proxies indicate that the HVMI, as a whole, have periodically higher depositional energies related to the LVMI. The oxygenation events were accompanied by elevated depositional energies at the seafloor, most likely related to the downward supply of oxic water by either currents or waves.

20 Once these higher energetic conditions ended, the supply of oxygen to the seafloor could not keep up with the oxygen demand of organic matter degradation, and the deeper waters became anoxic/euxinic. During these intervals, sedimentation was predominated by algal macerals delivered to the sediment as organo-minerallic aggregates and marine snow under quiescent conditions. The production of sulphide minerals (e.g. pyrite) and the accumulation of related sulphide forming trace metals was enhanced under these conditions, with the Fe being resupplied by a suboxic Fe shuttle that remobilised Fe through the chemocline. At times when Fe was not supplied, OM became sulphurised, which enhanced its preservation potential. Trace element enrichment was facilitated by a Mn/Fe particulate shuttle.

30 ~~Comparisons of trace element geochemistry show the studied section exhibits patterns similar to upwelling and anoxic basin type deposits. However, We~~ observe that the studied section bears similarity to the Landsort Deep of the present-day Baltic Sea in that a generally suboxic to euxinic system had periodic reoxygenation events.

In the context of the published chronostratigraphic framework, alternations between LVMI and HVMI occur on a short eccentricity (100 kyr) timescale. This is in line with the predictions presented by Armstrong et al. (2016), whereby an orbitally modulated expansion of the Late Jurassic Hadley Cell led to alternations between humid and arid climate conditions. We propose that the highly dynamic conditions in the studied intervals are representative of wet and humid conditions during which changes in continental weathering enhanced primary productivity and led to TOC enrichment. Conversely, the LVMI were deposited under arid conditions.

Supplementary Data

Supplement A: Details on sample preparation and analytical procedures.

Supplement B: Additional down-core trace metal (Cu, Zn, Cd) plots.

10 Supplement C: Mn/Al vs CaCO₃ content plot for the higher variability mudstone intervals.

Supplement D: Enrichment factors for studied section calculated relative upper continental crust (UCC: Rudnick and Gao, 2003).

Data Availability

Data will be made available to the public in a data repository.

15 Acknowledgements

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Figures

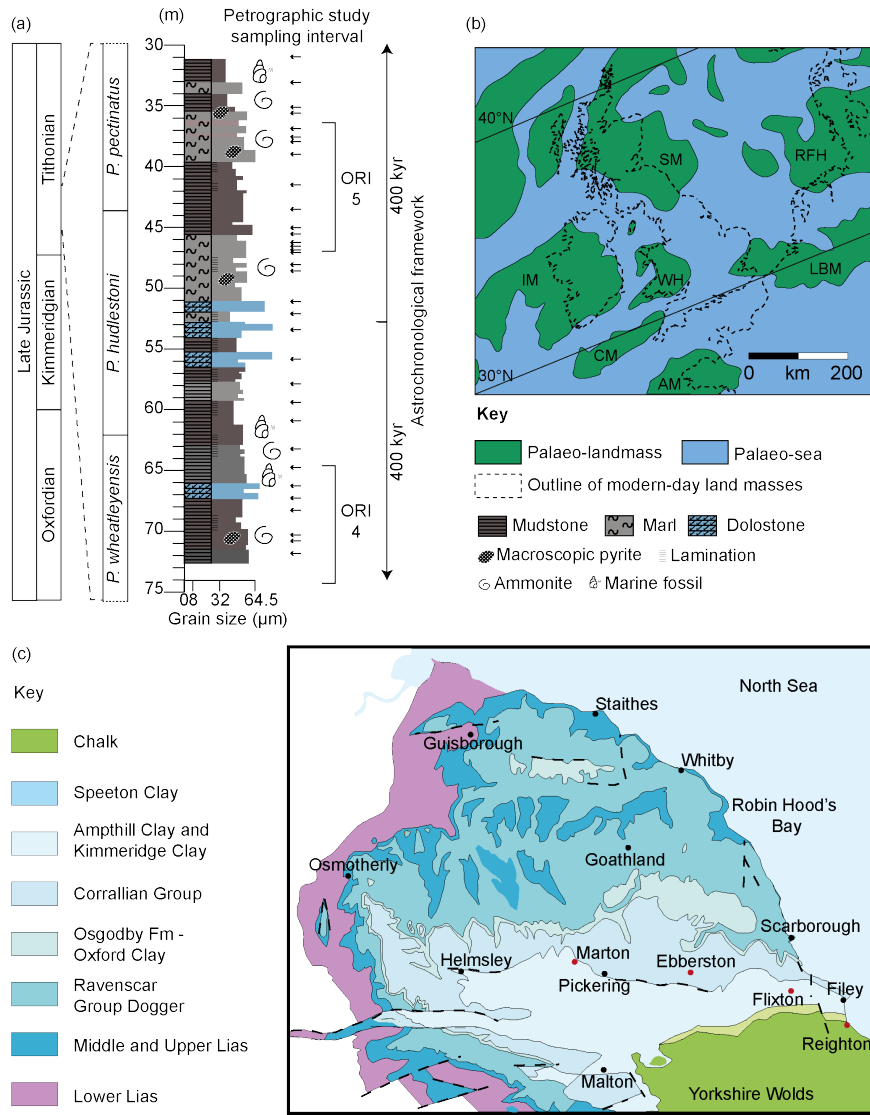
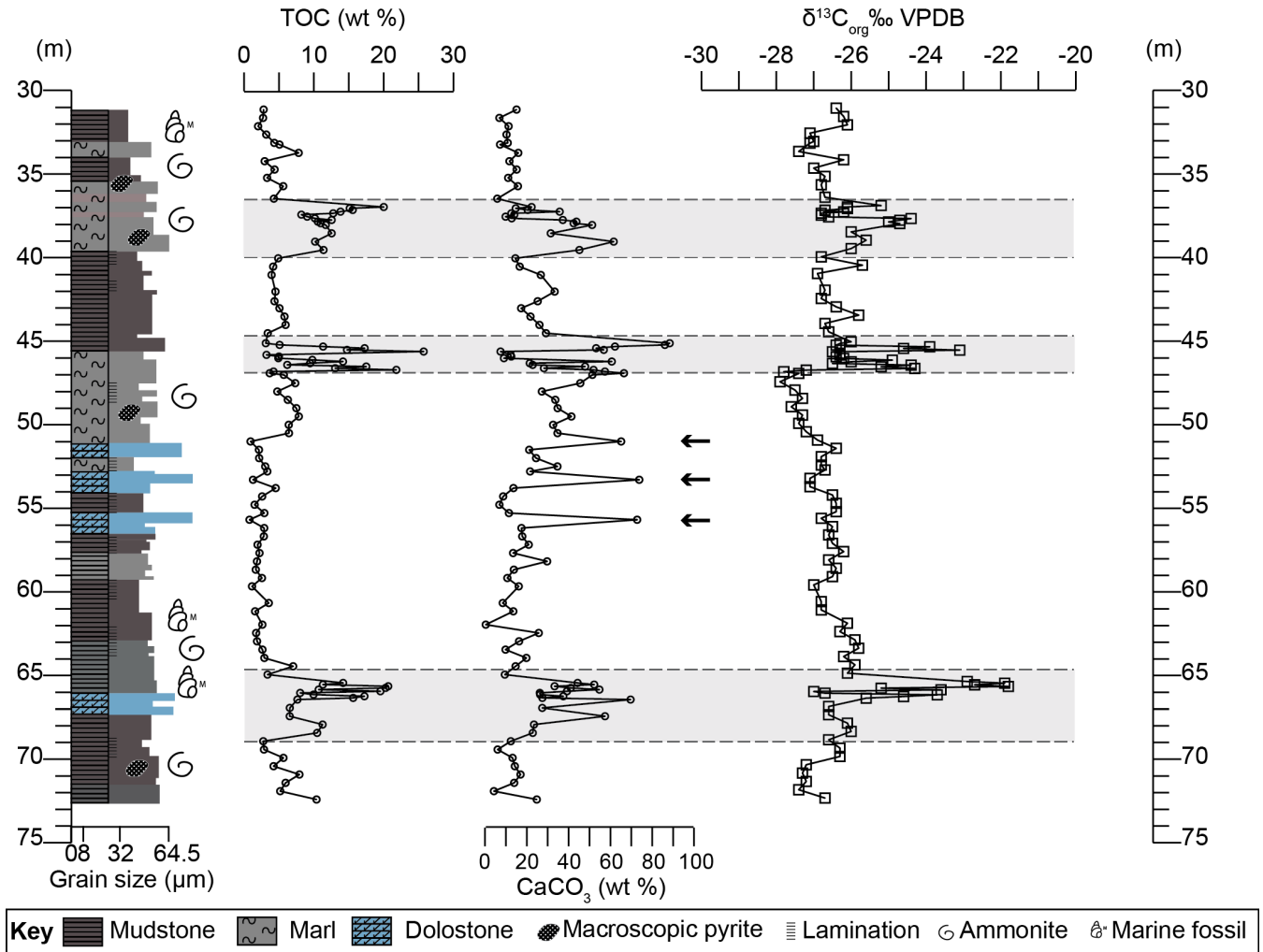


Figure 1: (a) Graphic log showing lithological variation of the studied section against geological time. See key for details. Horizontal arrows point to the petrographic study sample positions. Organic rich bands (ORBs) 4 and 5 as defined by Gallois (1979) [Astronchronology after Huang et al., 2010 and Armstrong et al., \(2016\).](#) (b) Palaeogeographical map ([modified from Turner et al., 2019.](#) after [Powell, 2010](#)). Solid black lines depict location of modern-day landmasses. (c) Modern day geological map of the

Cleveland Basin (after Powell, 2010). Red dots mark the location of the Marton 87, Ebberston 87, Flixton 87, and Reighton 87 boreholes.



5

Figure 2: Graphic log showing lithological variation of the studied section. Depth plots of total organic carbon (TOC) contents (wt %), calcium carbonate (CaCO₃) contents (wt %), and organic carbon isotope values (‰ VPDB). Grey panels depict the higher variability intervals (HVMI) defined in this study. Black horizontal arrows indicate samples with obvious diagenetic overprint.

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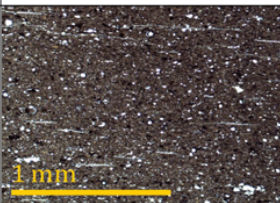
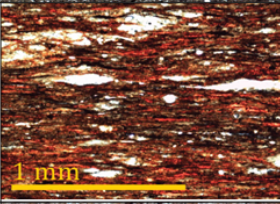
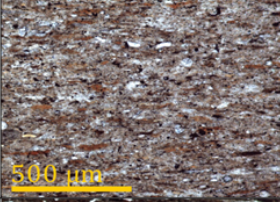
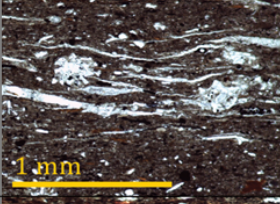
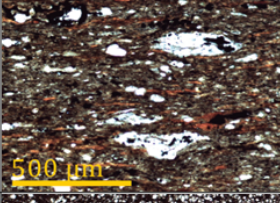
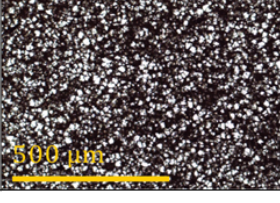
Name	Description	Interpretation	Optical light image
1. Clastic detritus-rich medium-grained mudstone	Well churned, argillaceous matrix. Abundant medium detrital grains and calcareous nanofossils which are commonly filled with authigenic kaolinite. Equant organic material grains sit within the matrix.	Deposited in a distal setting with a constant detrital input. Bioturbation indicates well oxygenated conditions with a moderate sedimentation rate allowing for extensive faunal colonisation. Organic material is commonly type III.	
2. Organic material and calcareous pellet-rich, laminated mudstone	Discontinuous wavy laminae are organised in to normally graded beds with erosional bases. Comprised of organo-mineralic aggregates, detrital material and calcareous faecal pellets.	Organic material was deposited as algal mats that were occasionally disturbed and locally reworked. Supply of detrital material was continuous. This facies represents the highest levels of primary productivity.	
3. Coccolith-dominated medium-grained mudstone	Fine to medium normally graded calcareous mudstone beds. Dominated by coccolith plates and coccolith-rich faecal pellets in a coccolith, clay mineral and quartz rich matrix.	This facies represents times of peak carbonate productivity. Continuous supply of detrital material that was diluted by coccolith material. Material was locally reworked in to graded beds.	
4. Biogenic detritus-dominated, fine to medium-grained mudstone	Disarticulated shell fragments dominate this facies. Shells and abundant fine to coarse mud-sized quartz grains sit within an argillaceous matrix. Diagenetic calcite stringers overprint.	Deposited when depositional energy was relatively high. Shells and framework grains brought in by unusual storm activity. Calcitic stringers were formed during early diagenesis.	
5. Agglutinated foraminifera bearing, medium to coarse-grained, carbonaceous mudstone	Well churned, argillaceous and algal material matrix. Detrital grains, abundant agglutinated foraminifera, and lithic clasts sit within the matrix.	This facies represent a finely balanced system between a well mixed water productive column indicated by the foraminifera and faunal colonisation, and the production and preservation of the algal material.	
6. Carbonate cemented, coarse-grained mudstone	Medium to coarse, angular, diagenetic carbonate grain-dominated sediment with an argillaceous matrix.	Dolomite rhombs formed during early diagenesis resulting from microbial sulphate reduction. These samples are discounted from paleoenvironmental interpretation.	

Figure 3: Summary table describing the six lithofacies identified in the petrographic study. Key descriptions and interpretations are noted for each facies along with a representative micrograph. All images are under plain polarised light. For further description see text.

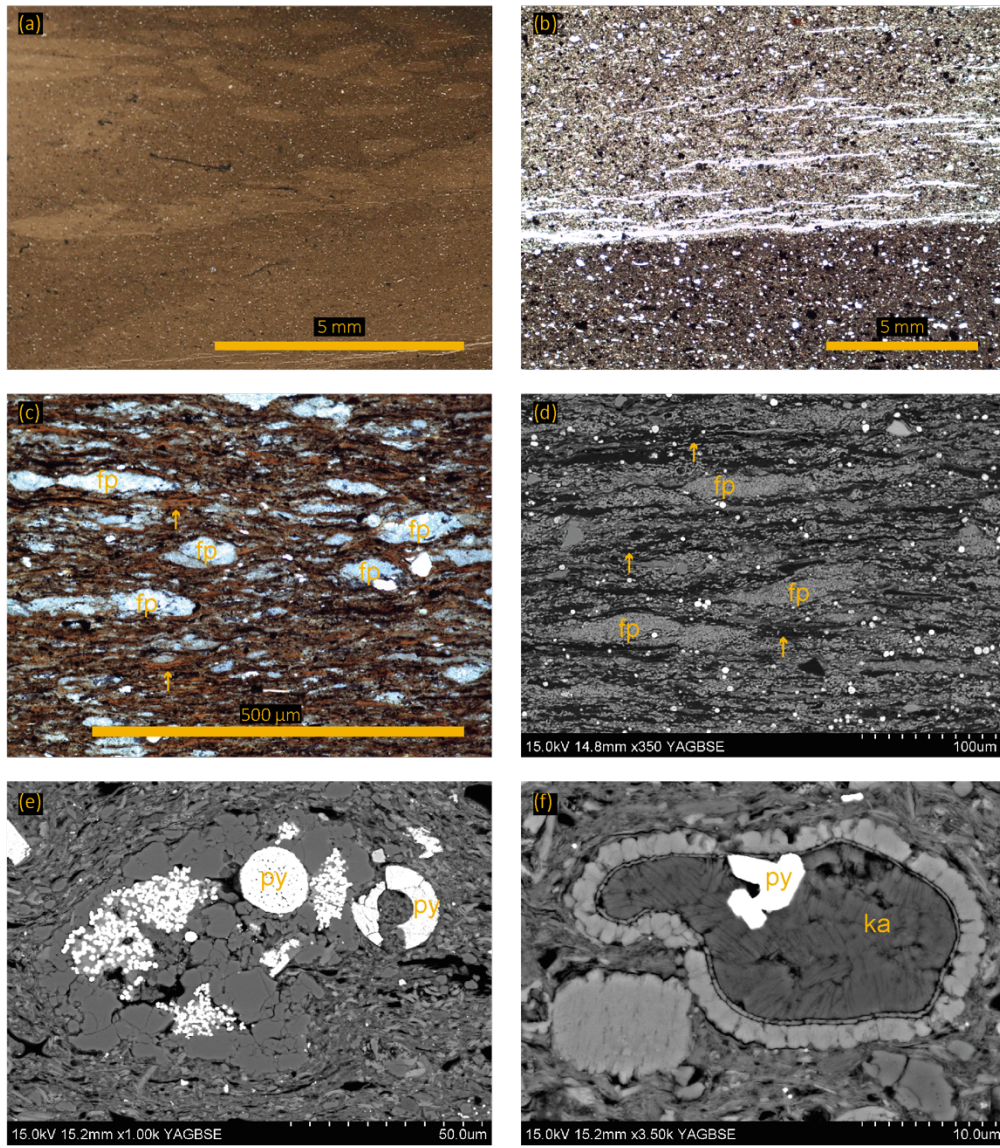


Figure 4: a) Photomicrograph showing a bioturbated sample (lighter patches are burrows). b) Optical micrograph of an erosional base. c) Optical micrograph showing faecal pellets (fp) and algal mats (yellow arrows). d) Same sample as in (c).
 5 Scanning electron micrograph showing faecal pellets (fp) and algal mats (yellow arrows). e) Agglutinated foraminifera with pyrite (py) both as framboids and as a replacement mineral. f) Scanning electron micrograph showing a calcitic test infilled with authigenic kaolinite (ka) and pyrite (py).

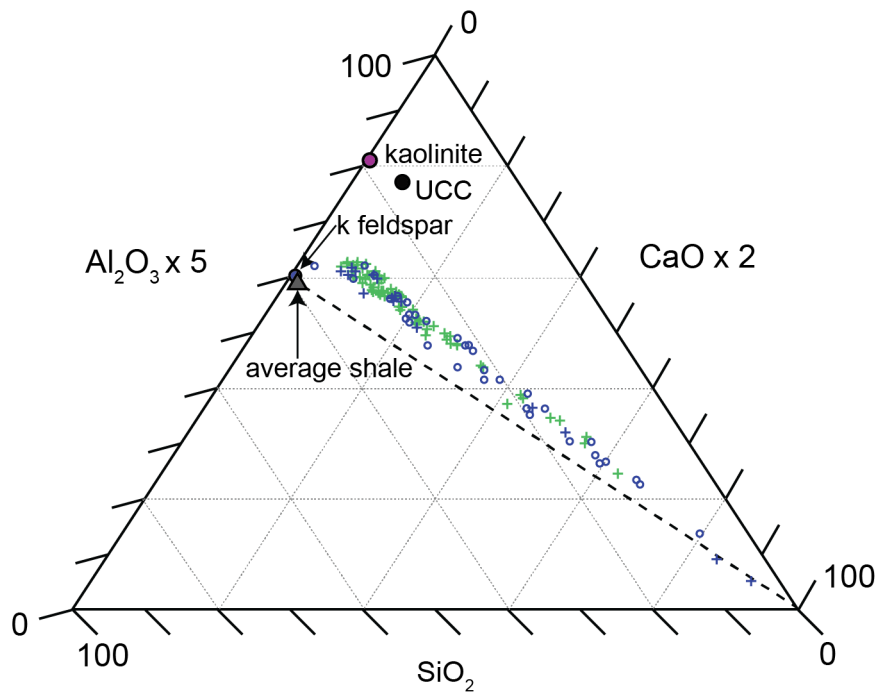


Figure 4 **Figure 5:** Ternary diagram (Brumsack, 1989) displaying the relative contributions of clay (Al_2O_3), quartz (SiO_2), and carbonate (CaO) within all samples. Lower variability mudstone interval (LVMI) samples are indicated by green crosses and higher variability mudstone interval (HVMI) samples are marked by blue symbols, TOC-rich samples ($\text{TOC} > 10 \text{ wt } \%$) are indicated by blue circles and TOC-lean samples ($\text{TOC} < 10 \text{ wt } \%$) are indicated by blue crosses. Axes are scaled to improve display of the data. Average shale (Wedepohl, 1991), upper continental crust (UCC; Rudnick and Gao, 2003), k-feldspar and kaolinite are plotted for reference. Dashed line shows the average shale-carbonate mixing line.

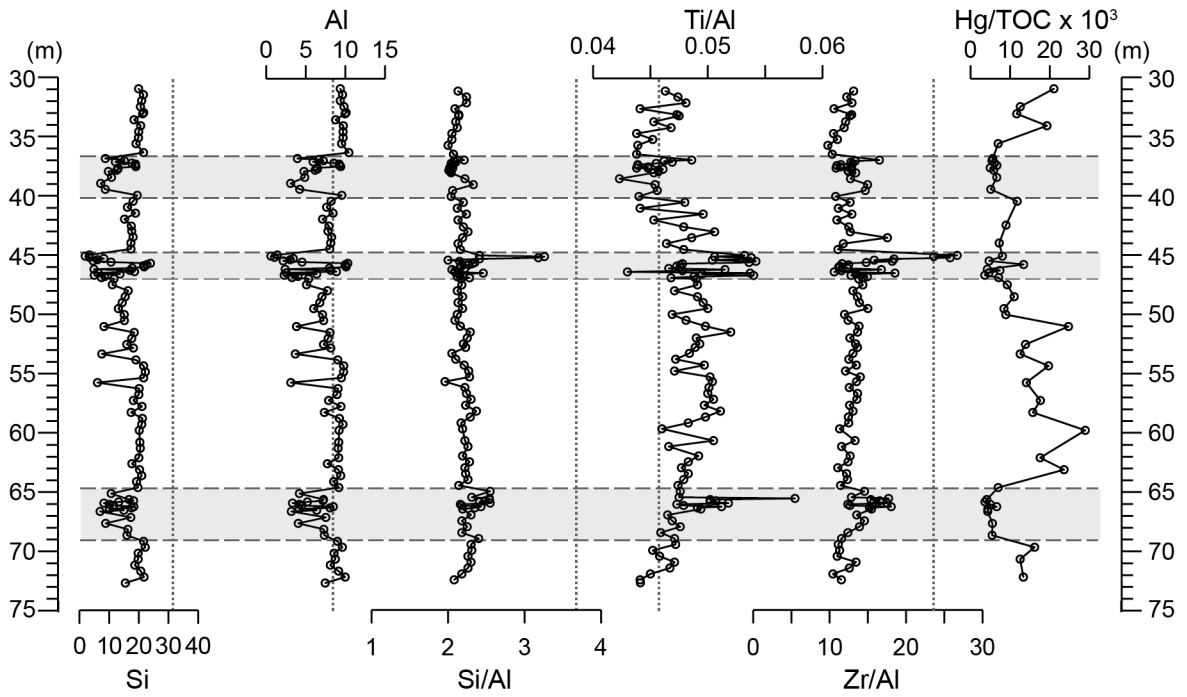


Figure 6: Depth plots of Al and Si concentrations, element/aluminium ratios, and Hg/TOC. Si (%), Al (%), Si/Al (%/%), Ti/Al (%/%), Zr/Al (ppm/%), Hg/TOC (ppm/%). Grey panels depict the higher variability mudstone intervals (HVMI) defined in this study. Vertical dashed lines represent upper continental crust (UCC) reference ratios.

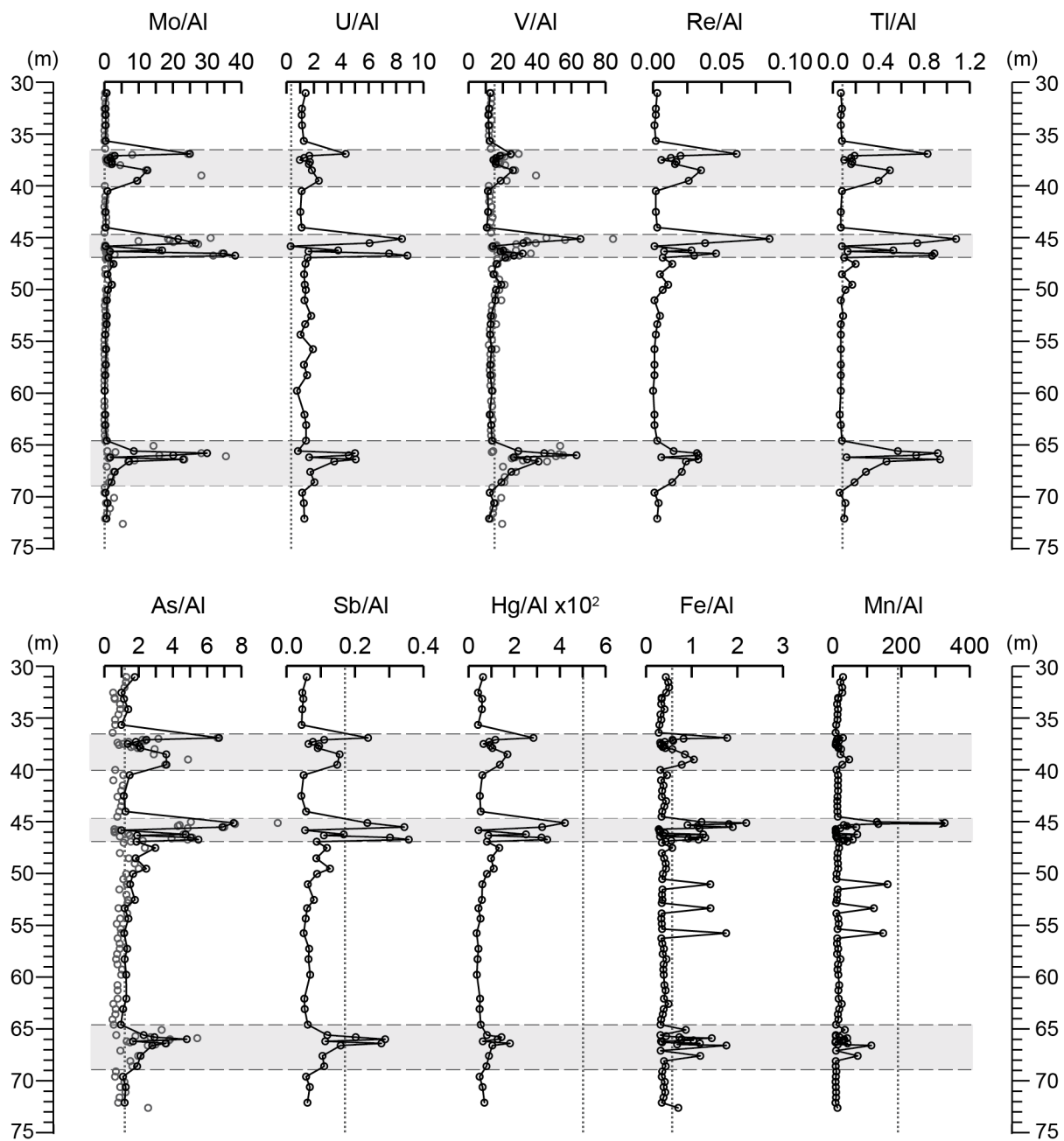


Figure 7: Depth plots of elemental ratios used as palaeoredox indicators. Mo/Al (ppm/wt %), U/Al (ppm/wt %), V/Al (ppm/wt %), Re/Al (ppm/wt %), Ti/Al (ppm/wt %), As/Al (ppm/wt %), Sb/Al (ppm/wt %), Hg/Al $\times 10^2$ (ppm/wt %), Fe/Al (wt %/wt %), and Mn/Al (ppm/wt %). Grey panels depict the higher variability mudstone intervals (HVMI) defined in this study. Where grey and black circles are seen on the same plot, grey circles mark the XRF data and black circles mark the ICP-MS data.

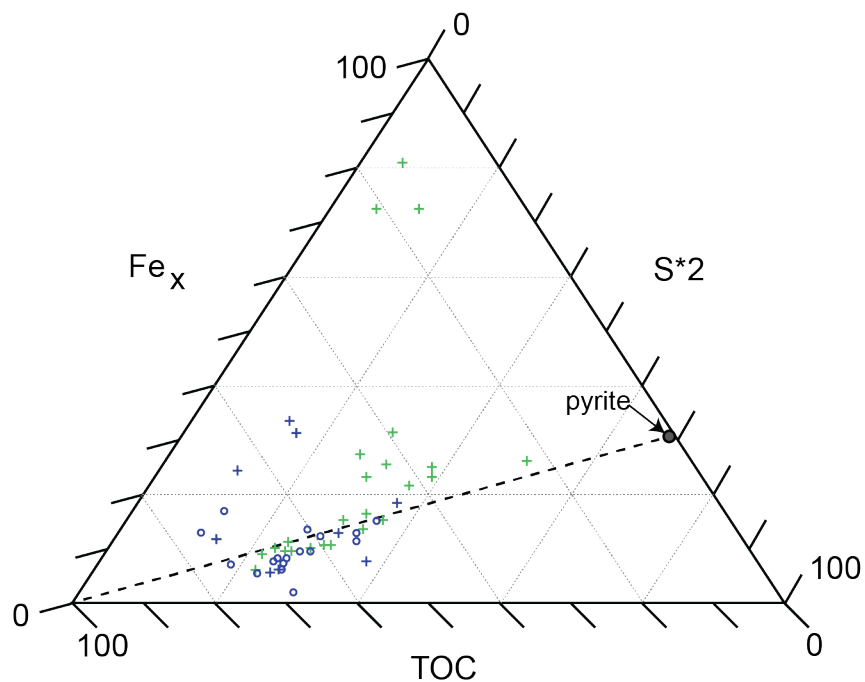
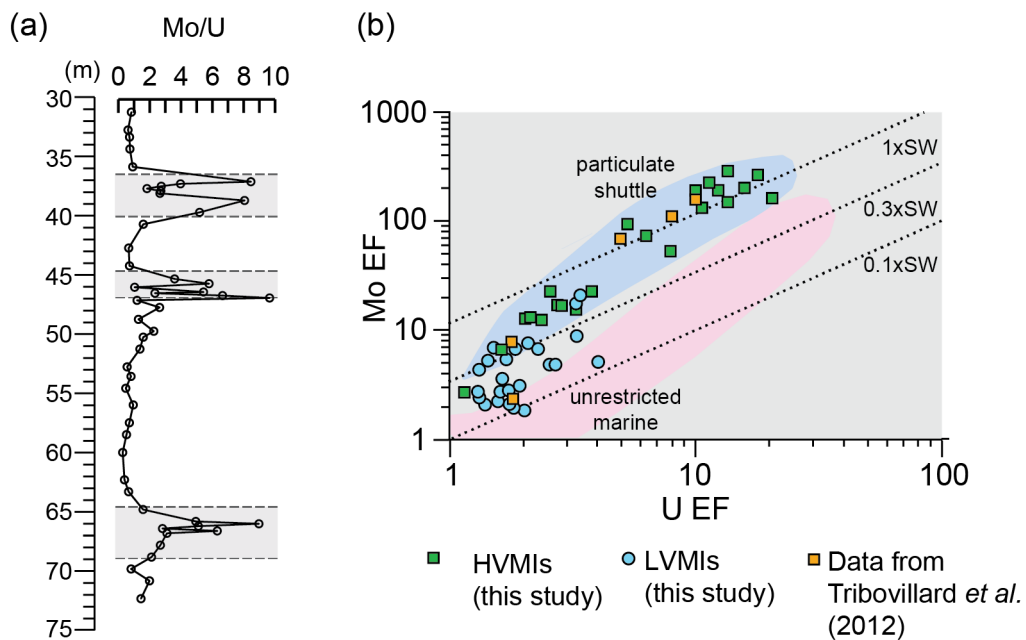


Figure 7: Fe_x -TOC-S Ternary diagram (after Dellwig et al., (1999); Hetzel et al., (2011)). See text for comments on Fe_x calculation. Dashed line represents TOC-pyrite mixing line. Lower variability mudstone interval (LVMI) samples are indicated by green crosses (three samples nearest to the Fe_x corner represent the diagenetically overprinted samples that were excluded from the interpretation). Higher variability mudstone interval (HVMI) samples are marked by blue symbols, TOC-rich samples (TOC > 10 wt %) are indicated by blue circles and TOC-lean samples (TOC < 10 wt %) are indicated by blue crosses.



5 **Figure 88:** a) Depth plot Mo/U (ppm/ppm) (after Algeo and Tribovillard (2009)). Grey panels depict the higher variability mudstone intervals (HVMI) defined in this study, b) scatter plot of Mo EF versus U EF calculated relative to Post Archean Average Shale (PAAS; Taylor and McLennan (1985) (after Tribovillard et al., 2012)). Lower variability mudstone interval (LVI) samples are indicated by blue circles, HVMI are indicated by green squares. Data from the Eberston 87 Core by Tribovillard et al., (2004) are represented by orange squares. Dashed lines are modern day seawater, 0.3 x modern day seawater and 0.1 x modern day seawater values shown for reference. The particulate shuttle is mapped in blue and unrestricted marine setting is mapped in pink. Axes are logarithmic.

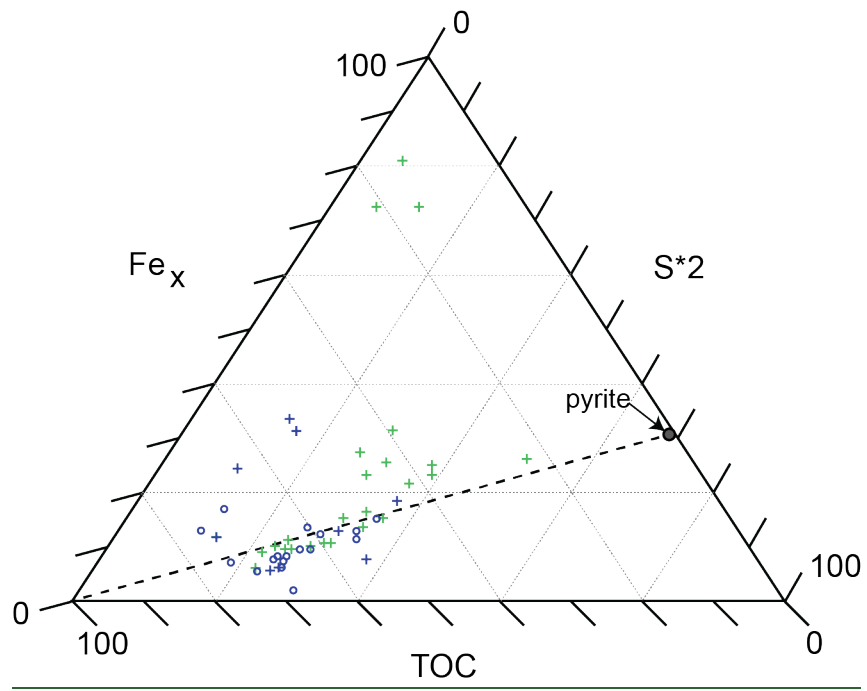


Figure 9:7: Fe_x-TOC-S Ternary diagram (after Dellwig et al., (1999); Hetzel et al., (2011)). See text for comments on Fe_x calculation. Dashed line represents TOC-pyrite mixing line. Lower variability mudstone interval (LVMI) samples are indicated by green crosses (three samples nearest to the Fe_x corner represent the diagenetically overprinted samples that were excluded from the interpretation). Higher variability mudstone interval (HVMI) samples are marked by blue symbols. TOC-rich samples (TOC > 10 wt %) are indicated by blue circles and TOC-lean samples (TOC < 10 wt %) are indicated by blue crosses.

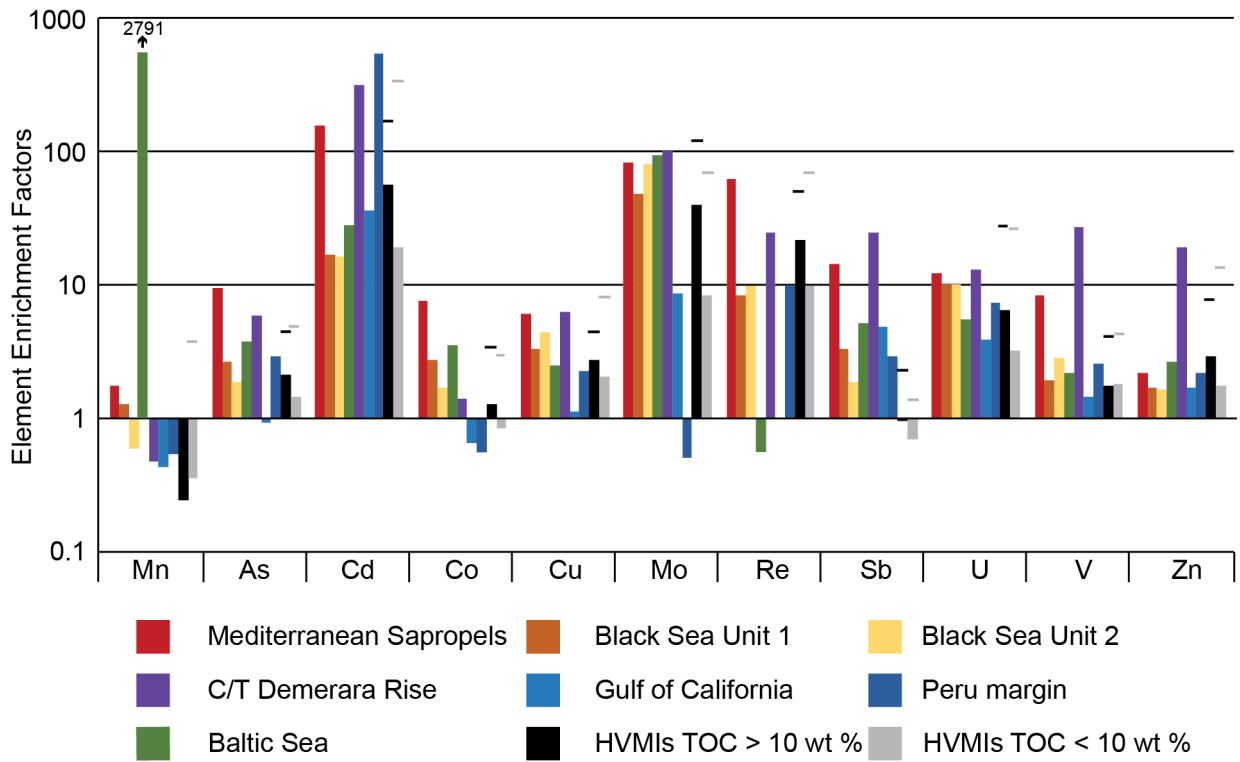


Figure 9 **Figure 10:** Bar chart illustrating enrichment factors (EF) for Mn, As, Cd, Co, Mo, Ni, Re, Sb, U, V, and Zn relative to average shale (Wedepohl, 1991) for Mediterranean Spropels, Black Sea Units 1 and 2, C/T Demerara Rise, Gulf of California, Peru margin (Brumsack, 2006), Baltic Sea (Dellwig, Unpublished data), and higher variability mudstone intervals (HVMI) from the present study. Maximum EFs in this study are marked by black lines.

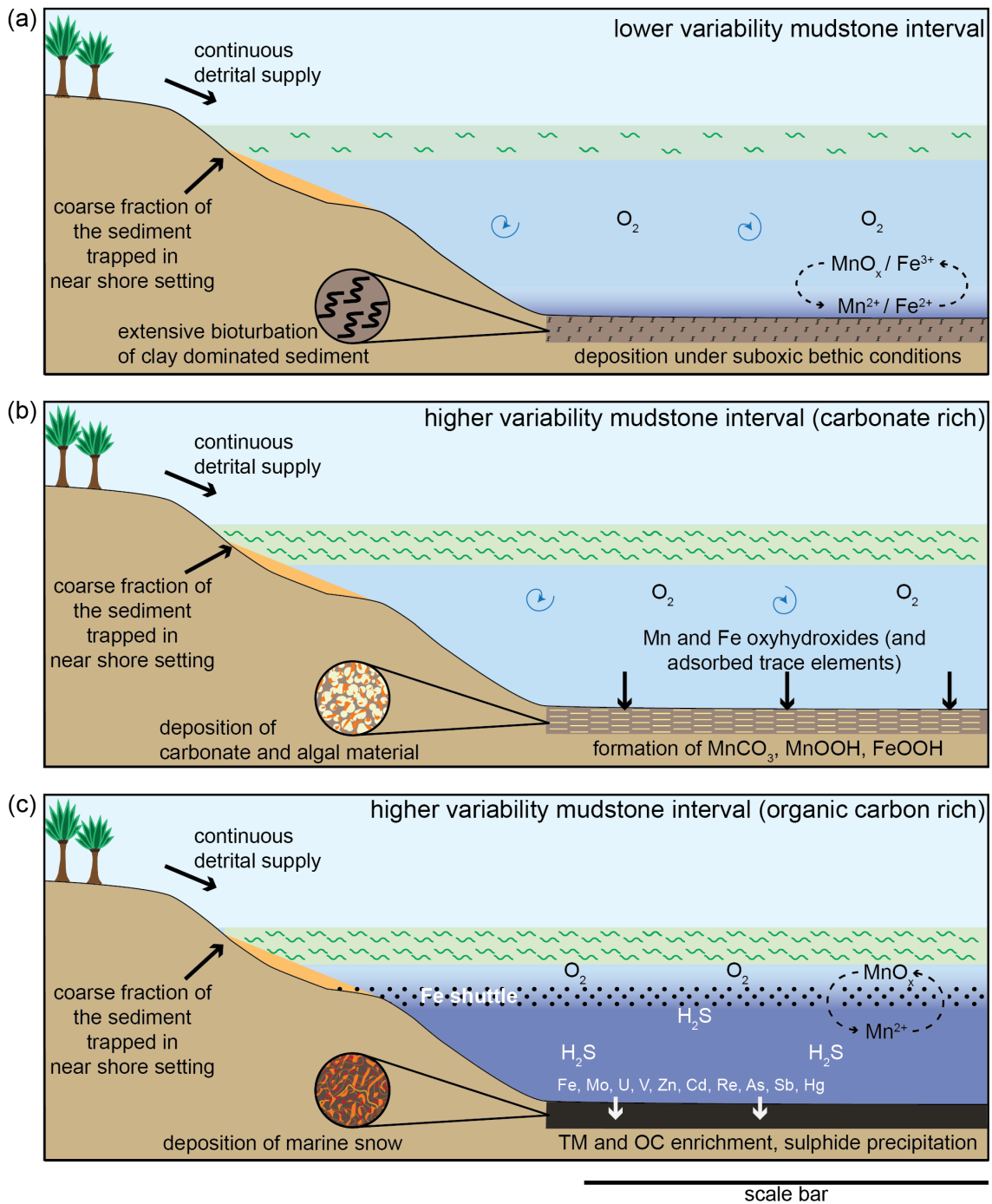


Figure 11: Schematic diagram illustrating depositional conditions during the different intervals of sedimentation. a) Lower variability mudstone interval, b) Periods of carbonate-rich sedimentation in the higher variability mudstone intervals, c) Periods of organic carbon-rich sedimentation during the higher variability mudstone intervals. Scale bar represents bathymetric lows, generally considered to be 10–100's km across.

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